Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 224 OCTOBER, 1937 No. 4

REPORT ON THE WORK OF THE BARTOL RESEARCH FOUNDATION, 1936–37.*

MADE TO THE MEMBERSHIP OF THE FRANKLIN INSTITUTE

BY

W. F. G. SWANN, D.Sc., Director.

INTRODUCTION.

As was the case last year, the report I now have to give centers around problems in what the physicist calls nuclear physics. The various atoms which constitute the elements of matter consist in each case of an external, more or less loosely bound, structure of negatively charged particles which we call negative electrons, and a central structure, the nucleus, which is positively charged, and which contains nearly all of the mass of the atom. The story of chemistry, of the emission of light, of X-rays and related phenomena, is the story of the external structure. The number of negative electrons in the external structure is equal to the number of positive electronic units of charge in the nucleus; but, the nucleus itself has properties other than those derived from this charge. The researches of the last few years have taught us that it is composed of particles of different kinds, some of them neutral particles known as neutrons. It is the nucleus which characterizes the atom and which, therefore, distinguishes the atoms from one another. If two nuclei differ

* Presented at the Stated Meeting held Wednesday, April 21, 1937.

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only in the number of neutrons which they contain, they will differ in weight but not in charge, so that, the external structure will be very much the same for each; and, it will be difficult to distinguish between them by chemical or optical means.

Atoms which differ from one another only in their weights are called isotopes of one another. The elements as they occur in nature are usually composed of mixtures of isotopes; and, until comparatively recently, it was almost impossible to separate these isotopes from one another because of the fact that chemistry knew no difference between them.

Our knowledge of the numbers and kinds of isotopes associated with the different elements has grown steadily during recent years; and, some of the most valuable and precise work in this field has been done in our laboratory by Dr. Kenneth T. Bainbridge, now on the faculty of Harvard University.

It may be well to remind you that physics is concerned with the use, properties, and activities of several atomic particles. First there is the negatively charged electron, then there is the positively charged electron, or positron, as it is called, which has a mass and charge equal to those of the negative electron. Then we have a neutral particle, the neutron, with a mass nearly two thousand times that of the electron, and the proton, which has a mass about equal to that of the neutron and a positive charge equal to that of the positron. Of course, the atoms themselves may be regarded as particles; but, one of them, the positively charged atom of helium, has been so active in atomic physics, as a sort of bombarding bullet shot out of atoms of more complicated structure, that it has acquired a name of its own and is called an alpha particle. The proton is really the nucleus of the ordinary hydrogen atom; but, it has an isotope of double weight which is called the deuteron, which also has performed services as an atomic bullet. I must not omit to mention the neutrino, a particle which has never been actually observed, but whose presence in the atom has been inferred by what we may call atomic circumstantial evidence. Finally, we have a class of particles—for it seems proper to so call them nowadays—known as photons. These photons

are the particle representatives of what we used to think of as waves in an all-pervading aether. They are particles varying in energy with the kind of radiation they represent. In the lower range of energies we have the photons which constitute light. Going to higher energies we have those associated with X-rays. With still higher energies we find the gamma rays from radium; and, with energies of the order ten thousand million times those of the photons for light we find the photons which figure in part in the phenomena of cosmic-rays.

INVESTIGATIONS ON NUCLEAR DISINTEGRATION.

Modern physics concerns itself in very large part with an investigation of the structures of the nuclei of the different atoms. For such purposes it is of importance to deal with the pure isotopes of the elements rather than with mixtures; and, it is, therefore, highly desirable to be able to separate these isotopes in weighable and usable amounts. Last year, I reported that Dr. L. H. Rumbaugh, who is working upon this matter at the Bartol Research Foundation, had perfected his apparatus to the point where he had separated into its two isotopes as much as four milligrams of lithium. At the present time, the apparatus is capable of separating out and collecting in usable form the isotopes of lithium to the extent of 0.1 milligrams per hour.

Dr. Rumbaugh has continued his separation of the lithium isotopes and has supplied samples of them to various research laboratories in the country for experimental purposes concerned with problems in atomic structure. In collaboration with the Department of Terrestrial Magnetism of the Carnegie Institution of Washington, and in particular with Dr. L. R. Hafstad of that Department, he has carried out an investigation upon the nature of the disintegrations produced by bombarding the lithium isotopes with high energy particles; and, I will first give a brief description of these experiments.

Disintegration Experiments on the Separated Isotopes of Lithium.[1]—It is customary to examine the structure of the nucleus of an atom by firing an atomic bullet at it, breaking

[1] This investigation has been published in full, see L. H. Rumbaugh and L. R. Hafstad, *Phys. Rev.*, **50**, 681 (1936).

it up, and examining what happens. The atomic bullets which have been use in the experiments of Drs. Rumbaugh and Hafstad are protons and deuterons. These particles are given their energy by subjecting them to voltages from 200,000 to a million volts. We are building an apparatus at the Bartol Foundation for producing high energies in particles; but, at the present moment we do not possess such equipment, and it is for this reason that Dr. Rumbaugh has availed himself of the courtesies extended by the Carnegie Institution in Washington in affording the use of their machine, which is designed for such purposes.

When the atoms of the elements are bombarded with high energy particles, various things may happen to them. They immediately may be persuaded to disgorge from the nucleus certain particles therein present. Or the atom which has been bombarded may be left in an unstable state, and long after the bombardment, as the atom counts time, it may break up spontaneously on account of this condition with the emission of certain of its constituents. Such atoms are, in fact, in the condition that radium normally is. The fact that the phenomenon is produced in the case I am discussing by bombardment results in its being termed "induced radioactivity." It is believed that sometimes particles emitted from the nucleus of an atom are actually created at the moment of what appears to be the emission.

Now the mathematical physicist has endeavored to understand all of these phenomena by building up what we call a theory of the atom, which simply amounts to his formulating for the atom a structure endowed with properties which are as few in number and simple in kind as are necessary to correlate all of the activities in which the atom participates. Formerly the physicist was not content unless his picture of the atom was that of something which worked in a manner similar to the things known to him in his everyday life, the dynamos, the steam-engines, the solar system, or what not. The complexities of modern atomic physics have necessitated his forsaking this ideal, so that he is now content if he can specify the properties of the atom in a purely abstract way. He is in the position of somebody who wishes to specify what heaven is like, for the purpose of understanding certain earthly

activities which he attributes to heaven; and who, having given up the picture of angels and harps, is led to describe it as a place where musicians are happy because they are provided with the internal satisfaction which on earth comes from appreciation by others, where the appreciation is proportional to their progress in their art, this progress being proportional to the amount of work they do. He adds some other properties to describe the happiness of the scientists and the interaction between the happiness of the scientists and the happiness of the musicians, and he tries to do all this in the simplest possible way consistent with the fact that all things happening on earth which may be attributed to the indirect activities of heaven may be accounted for in terms of those properties.

And so the physicist pictures for the nucleus of the atom what he calls a potential barrier, a kind of crater in the hollow of which the contents of the nucleus reside. He tries to picture states of agitation of the contents of that crater such as will permit some of the particles occasionally to emerge. He tries to set up what I may call laws of sensitivity of relationship between the walls of this crater, the things inside, and the disturbing influences of the external world such as are represented by electric forces, bombarding particles, and the like, and, he tries to do this in such a way that that which happens is contained as a consequence of the laws that he assumes. If this were all, he would be more or less wasting his time. If the structure which he created in his mind gave back to him no more than he put into it he would have gained little. The fact is, however, that having built his mental structure to deliver back to him the few phenomena represented by the experiments he has so far done, that structure forms the basis of an understanding of what may be expected under all sorts of other conditions, conditions which he may not be able to produce in the laboratory, but which may occur in nature—in the stars, for example.

It is for reasons such as the above that physicists bombard the atom; and Drs. Rumbaugh and Hafstad have bombarded the two isotopes of lithium with protons and deuterons of high energy. It is customary to denote these two isotopes as Li^6 and Li^7, the 6 and 7 indicating that the atoms concerned

are respectively six times and seven times as heavy as ordinary hydrogen. The main results obtained by Drs. Rumbaugh and Hafstad are as follows:

Under bombardment by deuterons which have received their energy under electrical potential differences ranging from 200 kilovolts to 1100 kilovolts, Li^6 emits two groups of protons of different energies At 540 kilovolts bombarding potential, one group has an energy permitting it to be capable of passing through 25.4 cms of air, while the other corresponds to an energy the equivalent of a path of 29.6 cms in air. No such groups of protons were obtained, however, on bombarding Li^7. This fact indicates the importance of working with the individual isotopes, since, had ordinary lithium been used, there would have been a much greater ambiguity in interpreting the emission of the protons. Again under deuteron bombardment, with energy corresponding to 200 kilovolts or more, Li^6 was found to emit neutrons. On the other hand, Li^7 was rendered radioactive with a half life period of about 0.5 second, the radioactivity being such as to result in the emission of beta rays, which are negative electrons. Li^6 showed no radioactivity under bombardment. When the isotopes were bombarded by protons of energy corresponding to 450 kilovolts and to 1000 kilovolts, Li^7 emitted gamma rays, but Li^6 gave no such emission.

It would take us too long to enter into the theoretical significance of these results; and, indeed, the development of the theories and the accumulation of experimental data are at present going hand in hand. The experimental data form the basis of material out of which theories are built and every additional fact is an aid to the further development of the theoretical structure.

After completing the foregoing investigations, Dr. Rumbaugh proceeded to manufacture some more samples of lithium; and, for the last few weeks has been in Washington exposing them to the bombardment of high energy particles. I wrote asking him to send me a brief statement of his results which could be incorporated in my report this evening. I have just received an eight page letter with four large charts, each containing about a dozen curves; and, I have been pondering on the question of how I could digest the signifi-

cance of all of this to you. I can do so only in the most general terms.

When the chemist wishes to ascertain the structure and properties of a compound, he treats it with different chemicals, finds out what occurs, and builds up for that unknown compound a structure which harmonizes it with experiments in terms of the general principles of his subject. As rather crude analogies to these various chemicals with which the chemist treats his unknown compound, we have for the physicist a number of different bombarding radiations of the kind of which I have spoken. Sometimes the chemist heats his testing reagents so as to vary the effects produced and in terms of these variations predicts his conclusions. As analogous to this, we have the physicist bombarding the nucleus of the atom with rays of varying and known energy. If he assumes a certain structure—in the modern sense of the word—for the atom which he is bombarding, he can sometimes predict what the result of the bombardment will be as regards secondary particles which are hurled out of the atom; but, frequently there is a certain amount of ambiguity in the prediction of the whole story depending upon uncertainties of different degree in the nuclear structure which he assumes. This ambiguity is only to be removed by trying various hypotheses and testing their conclusions in comparison with experiments. To take an example, if one assumes for the lithium atom a certain type of structure and imagines the atom bombarded with deuterons, a condition may be expected in which the atomic forces of the system result in the deuteron being relieved of a proton at impact with the atom, with the result that the remaining neutron is able to surmount that wall which guards the nucleus and enter the atom. As a matter of fact, a neutron relieved of an accompanying proton is something like a group of revolutionaries relieved of their voiceful agitators. It is able to get through the guards which preserve the constitution of the system, and once inside, promote a revolution by claiming for itself a place such that nothing but a complete break up of the atom can provide for the accommodation. Under these conditions, the laws of atomic physics tell us something about the nature of the revolution which will occur and of the type of particles which will be

hurled out of the nucleus in the conflagration which results. On the other hand, it is possible to conceive a situation in which the neutron enters the nucleus with its accompanying proton. The story of the actual disintegration is determined largely by which of these two processes occur. Now, it is possible to decide between these two questions; for, if the former process occurs, some energy must be provided for the neutron to enable it to discharge the agitating proton before entry into the atom. The proton demands payment for its resignation from office. This payment comes from the kinetic energy of the pair—of the deuteron; and, if the physicist has not given the deuteron enough kinetic energy to provide for the payment, the proton can never be persuaded to leave its partner. Thus, if we are to assume that the atomic disintegration does occur by the entry of the neutron into the atom after release of its partner, we shall have to conclude that no disintegration can be produced by deuterons which have initially less kinetic energy than is necessary to provide for the payment aforesaid. On the other hand, if we find that atomic disintegration can be produced by deuterons of any energy, even though the efficiency of such disintegration may be reduced by the reduction of the energy, we must conclude that it is the deuteron as a whole which enters the nucleus and that, therefore, it is the action associated with that event which is the one subsequently to be expected. Now, Dr. Rumbaugh and those working with him have found that disintegrations can be produced by energies far less than that necessary to dissociate the deuteron, so that the second process which I have cited is the one in harmony with the experiments. It is found, moreover, that in the actual disintegration all sorts of particles are emitted, protons, alpha particles, electrons, neutrons, gamma rays and helium nuclei. It is from an examination of the bricks which have fallen from this bombarded structure that one has to build up a concept of how that structure must have been formed to produce the debris which has resulted from it.

The Cyclotron.—The investigations I have already cited emphasize the importance of realizing means for producing high energies in atomic particles. The most obvious way to produce such energies is to start with charged particles and

to cause them to acquire their energies under a large difference of electrical potential. It was in this way, in fact, that the particles used by Drs. Rumbaugh and Hafstad were given their energy; and, the potential differences there involved were never higher than about one million volts.

It is of the greatest importance to perform such experiments at much higher energies, energies ranging up to ten million volts and even more, if possible. When one starts to devise a piece of apparatus in which there are two parts at a difference of potential of ten million volts one encounters a situation in which, unless the apparatus is housed in an enormously large room, sparking will occur to the walls of the room. Nothing short of a building comparable in size with a dirigible hangar is practicable [2] and even then the apparatus itself is apt to assume enormous proportions. It is for this reason that another device known as a cyclotron has been invented by Professor E. O. Lawrence of the University of California, whom I am proud to claim as an old student at Minnesota, later at Chicago and then at Yale.

Professor Lawrence's device is probably the most satisfactory for the purpose of any yet designed. It is coming extensively into use in all parts of the world; and, ten at least, have been or are being built in this country.

High energy particles are of use not only in investigations concerned with pure physics; but, they are becoming of increasing importance in the treatment of disease, not merely in direct treatment, but also in the production of sources of induced radioactivity, which sources can perform, and with greatly increased latitude of use, those functions performed formerly only by radium and a few other substances of the kind. It is possible now to produce as the result of a day's bombardment with such beams of rays as one can obtain from the cyclotron an amount of radioactive material which, in its activity, is the equivalent of a quarter of a gram of radium. It is true that many of these induced radioactive substances have but a short life; but, one can produce more when that which has been made has died; and, a short life has many advantages in certain cases. Thus, if one should inject

[2] I exclude for the moment devices in which high potentials are produced and used under conditions of very high vacuum, or very high pressure.

ordinary radium into the blood stream for some beneficial purpose, even if it should perform that purpose it would then proceed to devote the remainder of its activities to killing the patient. Since the radium is only half dead in two thousand years, the patient would be liable to lose out. With a radioactive material of half life of a few days or even a few hours, the good work may be performed and the evil work omitted. Then again, the existence of these short-lived induced radioactive substances permit such investigations as the following:

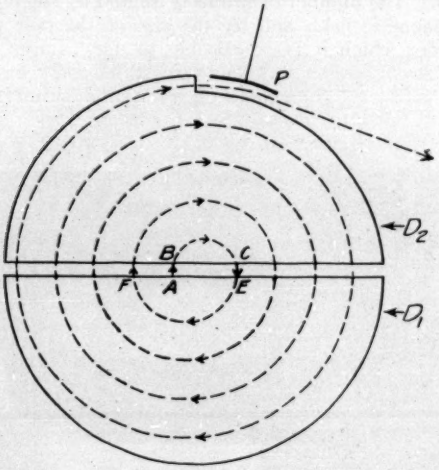
If we wish to know how long it takes for the element sodium, for example, to be transferred from one part of the body to another through the blood stream it is possible to inject a little of the radioactive sodium into the blood; and, by means of sensitive devices which can detect it through its radiations, find just where it goes and how long it takes to get there.

It is for such reasons as the foregoing that the Biochemical Foundation of The Franklin Institute, of which our good friend, Dr. Ellice McDonald, is Director, has felt the desirability of adding the potentialities of the cyclotron to those of its other very excellent equipment; and, it is installing such a cyclotron in the laboratory of the Bartol Research Foundation at Swarthmore, where it will be used in part for biological problems and in part for problems in pure physics. Dr. A. J. Allen has spent some time with Professor Lawrence at the University of California, and has been in immediate charge of the erection of the cyclotron. In this he has been assisted by Mr. Milo B. Sampson.

Instead of imparting velocity to a particle by a single blow, as is accomplished in the utilization of very high potential differences, the cyclotron performs its function by imparting the energy in a large number of small kicks. The general idea is as follows: D_1 and D_2, Fig. 1, are two semicircular portions forming a hollow pancake. A charged particle produced in a manner which I need not describe may be considered as starting at A. A relatively small potential difference of 50,000 volts kicks it across to B. Now the D's are between the poles and the magnet, whose field may be regarded as perpendicular to the paper. Under these conditions it is well-known that the moving particle at B describes

a semicircle and comes to C. If the 50,000 volts had remained fixed, the particle would now proceed to cross the gap to D_1 at E. It would be opposed by the electric field and would lose all the energy it had gained in its first kick. How-

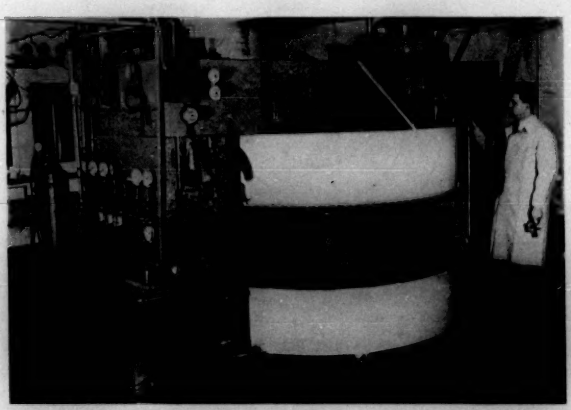
FIG. 1.



ever, the 50,000 volts is not constant; it is arranged to be of an oscillatory nature of such period that, by the time the particle has traveled from B to C, the field has reversed, so that, in crossing to D_1 at E the particle's energy is still further increased. On arriving at E it describes another semicircle under the influence of the magnetic field. It turns out that this semicircle is of larger diameter on account of the higher energy; but, it turns out that the increase of speed of the particle enables it to describe the semicircle of larger diameter in the same time that it took for the first semicircle, so that it arrives at F just in time for the electric field, which is again reversed, to give it a further kick across to D_2. The particle goes round and round spiralling outwards in this manner, acquiring more and more energy until it finally emerges at

the edge of the D's. A charged plate P serves to perform the final deviation which brings the particle outside the D's. The energy which it acquires is, of course, equal to the energy acquired in a single crossing of the D's, multiplied by two for the return journey and multiplied by the number of spirals provided. The number of spirals is limited by the magnitude of the magnetic field, and by the size of the pole pieces of the magnet which it is practicable to use. Large magnets are necessary; and, being electro-magnets, they have to be supplied with large currents of electricity and suitably cooled.

FIG. 2.



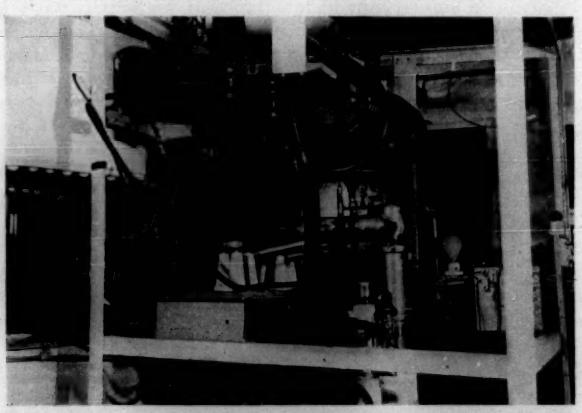
The circular white portions contain the coils which excite the electromagnet whose pole pieces lie parallel to and between the planes of those coils. Dr. A. J. Allen stands beside the apparatus.

Figure 2 is a picture of the cyclotron which is now being completed in the Bartol Foundation. Its total weight is 80 tons; and, it is expected that it will produce deuterons of energy eleven million electron volts and protons of energy fifteen million electron volts. Fig. 3 is a picture of the oscillator used for generating the oscillating electric field.

Improvements in Geiger-Mueller Counters for Various Purposes.—I have had frequent occasion in former reports

to refer to the Geiger-Mueller counter, which is a device for detecting high energy charged particles, including photons, such as occur in experiments on nuclear physics and in the field of cosmic-rays. It will be recalled that in its simplest form the counter comprises a metal tube inclosed in glass

FIG. 3.



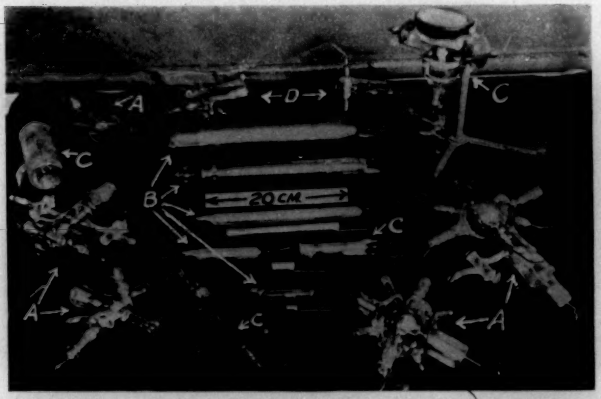
The oscillator need not be described in detail. The coils which couple the oscillator to the *D*'s are seen between the upper and lower coil housings. Since this report was presented, the coupling system for the creation of the potential difference between the *D*'s has been modernized by utilization of the transmission line principle.

containing some gas at reduced pressure. Along the axis of the tube is strung a fine wire. When a suitable potential difference is applied between the wire and the cylinder, the passage of a charged particle through the latter precipitates an electric discharge which may be amplified and caused to record itself in any desired manner. Sometimes, as in the case of photons, the particle—the photon—does not precipitate the discharge directly but through the agency of a charged particle emitted from the metal tube. Under such conditions the appliance usually counts only a comparatively small fraction of the photons which fall upon the cylinder. The factor of proportionality depends upon many considerations, the nature of the cylinder surface, the nature of the gas, etc.

Two or more counters used in tandem can act as a kind of telescope for high energy particles in being made to record in their combined action only those rays which pass through all of them.

With the growth of nuclear physics and the study of cosmic-rays, the importance of counters has increased at a rapid rate; and, hand in hand with the greater precision desired as knowledge has advanced, have gone more and more exact-

FIG. 4.



Collection of Geiger-Müller counters for measuring various weak radiations. They are (*A*) photon counters; (*B*) gamma ray, cosmic ray and x-ray counters; (*C*) beta-ray and soft x-ray counters, which are also suitable for measuring particles from nuclear interactions; (*D*) experimental multiple counters in single glass envelopes.

ing requirements upon the counters themselves with greater and greater demand for reliability and precision of performance. Dr. G. L. Locher has devoted much attention to the study of counters. He has devised many forms, and has given special attention to this matter during the last year. Fig. 4 is something like the glassware department of a ten cent store. It is a conglomeration of counters of various types which Dr. Locher has devised for various purposes. I, naturally, cannot describe them all in detail. It will suffice

to cite some of the considerations which have been involved in the study and design of these counters.

An ideal counter is one which should never give a false indication as the result of some disturbance other than that produced by a ray passing through it. Moreover, it should record every ray which does pass through it regardless of the path taken by that ray in the counter itself. After the passage of a ray, a time for readjustment in the counter is necessary before it is ready to record another. This time should be as short as possible. In cases where counters are used for recording photons, the efficiency of emission of the charged particles from the walls of the counter tube by the photons should be as great as possible, and should remain invariable in magnitude. Some of the radiations which are encountered in modern studies of nuclear physics and some encountered in the field of cosmic-rays are of such small penetrating power that they can only pass through very thin layers of material. For this reason, counters designed to observe them must be provided with very thin walls, particularly when the nature of the observation is such as to require the use of two counters in tandem. It is even desirable to go to the extent of combining the functions of the metal cylinder and that of the glass container into one unit by painting the former upon the inside of the latter, which then is made as thin as possible. Such a process is apt to introduce difficulties of its own, because such a painted cylinder is not endowed with the best of electrical conducting properties, so that extra precautions become necessary to permit it to perform the two-fold function which it performs in an ordinary counter, the function of acting as one of the electrodes for the discharge and the function of shielding the interior from external electrostatic disturbances.

In providing for the foregoing conditions attention must be given to the pressure and general condition of the gas used. Strange to say, most absolutely pure gases are not desirable, since counters made with them do not function properly. What happens is that after a ray has initiated a discharge in the counter that discharge perpetuates itself, so that the counter cannot recover in preparation to record another ray. There was a time when it was believed that the gasses to be

used in counters should be as pure as possible with only a very small amount of carefully selected contamination. Dr. Locher's researches lead to the conclusion, however, that impurity, of almost any kind within the range of his investigations, is a more desirable characteristic than purity, and that a counter is not very sensitive to the kind of gas that it contains. In the case of photon counters the treatment of the surface of the cylinder and the nature and pressure of the gas has a profound effect upon the efficiency of the appliance. It would take too long to enter into all these questions which are matter of detail and which are in preparation for full publication elsewhere.

Neutrons play a very important part in modern atomic physics; but, being uncharged, they do not affect the counters directly. It is customary to detect the number of them which have fallen upon some assigned piece of metal in a certain time by estimating the amount of induced radioactivity which they produce in that element. It is convenient to make the cylinder of a counter out of the element used as an intermediary detector in this connection. Silver is a convenient element for the purpose and has been used in some of the counters which Dr. Locher has constructed for this purpose. Strange to say, one must be careful as to the kind of glass used since the Boron in Pyrex glass, for example, has itself a strong absorbative effect on the neutrons. When using a counter for detecting induced radioactivity in this way, very rapid counting is involved and special circuits of rather complicated design are necessary.

Dr. Locher has here a silver counter which presently we shall render radioactive by bombardment with neutrons, these neutrons being produced by the bombardment of beryllium with alpha rays from radium. At present the counter-wall is non-radioactive and such impulses as it records are produced by accidental circumstances, cosmic-rays and so forth. Dr. Locher will now transfer the counter to another room where the neutrons are produced and subject it to their bombardment. He does this in another room because he does not want to render the audience radioactive. In about five minutes he will bring it back and if all is well,

its activity will be indicated by its having acquired the power to operate the recording device upon this apparatus.[3]

Dr. Locher has given special attention to new types of photoelectric counters, particularly with a view to extending the range of their response and of increasing the sensitivity of that response. Here is a counter which is coated with thallium. At present it is covered up. If we uncover it, it will, as you observe, operate very rapidly from the lights of the room, so we must turn them out. If not illuminated by my lecture, it will now remain silent. An assistant will now strike a match at the far end of the room, and, as you see, the counter knows all about it.[4]

INVESTIGATIONS ON COSMIC-RAYS.

During the last year we have continued to devote considerable attention to the study of cosmic-rays. In former reports I have been accustomed to introduce our researches in these matters by a preliminary survey of the whole cosmic-ray problem. On the present occasion I must curtail this survey to the minimum and it will suffice to remind you that as the result of extensive investigations extending over the last twenty-five years we have come to the belief that there is a radiation of very high penetrating power entering our atmosphere from outside. The suggestions as to the nature of this investigation divide themselves into two categories. First, we have those which regard the radiation as composed of photons, which in the present instance are to be regarded as of the nature of X-rays of such penetrating power that if they were produced in an X-ray tube that tube would have to be supplied with potentials of an order ranging between a hundred million volts and ten thousand million volts. The second suggestion is that the rays are material particles; and, in this class of suggestions is to be found the main one to the effect that they are charged particles. The decision on such matters is complicated by the fact that our knowledge of all of these types of radiation is such as to suggest that any one

[3] This experiment was carried out as described, and the production of the induced radioactivity was demonstrated.

[4] This experiment was carried out as described, and gave a pronounced response to the match at a distance of approximately 80 feet.

of them on entering the atmosphere would give rise to all of the others, so that observations on what is actually to be found in the atmosphere do not give very direct evidence for the decision of what comes in. In order to make this decision, an examination must be made outside of the atmosphere where man cannot go. Fortunately, nature has provided some apparatus to discriminate between the possibilities. She is doing the experiment continually and leaving mankind to interpret the results. The apparatus which nature has provided is a great big magnet. It is that magnet which is our earth. Its influence extends in appreciable amount for thousands of miles into space and since charged particles moving in a magnetic field are deflected by that field, variations of intensity with latitude are to be expected if the incoming particles are charged. I have traced this matter in some detail in former reports. The latitude effect was discovered by J. Clay and established on a firm foundation by the investigations of A. H. Compton and others. It is being re-studied in modified form by Dr. T. H. Johnson of our laboratory, who has continued those experiments which I described last year, in which an automatically recording Geiger counter apparatus was mounted upon a ship which traveled back and forth over a wide range of latitude.

Associated with the latitude effect is a directional effect which results from the fact that, for positively charged particles, for example, radiation from the west is to be expected of greater intensity than that from the east. The opposite effect is to be expected for negatively charged particles, so that the actual existence of such an east-west effect implies an excess of one kind of particle over the other. The reality of this east-west effect was established by T. H. Johnson and J. C. Street, and independently by A. H. Compton and L. W. Alvarez on the basis of experiments cited in my former report.

An examination of the latitude and directional effects has led those who support the charged particle hypothesis to the view that at least thirty or forty per cent of the incoming primary radiation must be attributed to charged particles and the data are consistent with the view that all of it may be regarded as of this type.

The Corpuscular Theory of Cosmic-Rays.—I have devoted

considerable attention to a study of the charged particle hypothesis and to the developments which must be made in it to permit it to represent the facts. These ideas, to some of which I have referred in former reports, have during the last year been welded together into a more consistent whole and are set forth in a communication which was made to the Harvard Tercentenary Conference last summer.[5] Briefly, the situation is this:

Confining our attention to vertical rays, the earth's magnetic field possesses the power to block the entry of charged particles into the atmosphere unless their energies are above a certain limit which depends upon the magnetic latitude. For electron rays, those rays having energy less than 17×10^9 e.v., would be unable to enter at the magnetic equator. At 41° magnetic latitude the lower limit of energy for entry is 6×10^9 volts. At 50° it is 3×10^9 volts, and so on, diminishing as we approach the poles. If the rays lost their energy by ionizing the air through which they passed, that is, by detaching electrons from the exterior structure of air molecules, and formerly this was believed to be the only method by which they could lose energy, an electron ray would lose only 10^9 electron volts in passing through the atmosphere, so that, at the equator, where a ray has to have seventeen times this energy to get in at all, we should have a situation in which any ray which succeeded in making entry to the atmosphere through the earth's magnetic field would pass right through the atmosphere and far into the earth before it was stopped. There would, therefore, be no variation of the primary vertical intensity with altitude in equatorial regions. It would not be until we reached magnetic latitudes as high as 60° where the energy for entry is 10^9 e.v. that we should get any variation with altitude at all. In fact, variation with altitude would have to be attributed entirely to the rays whose energy was less than 10^9 volts, but greater than the energy of entry, and therefore, could not occur at all where the energy of entry was greater than 10^9 volts. At sea-level we should experience the situation in which, as we went northward or southward from the equator, the intensity increased because the lower limit of entry was

[5] W. F. G. Swann, *Phys. Rev.*, **50**, 1103 (1936).

reduced with increase of latitude, permitting more and more rays to enter. This increase would go on until the magnetic latitude 60° was reached and there the increase with further increase of latitude would stop since the rays which can get in above 60° and not below it could not penetrate to the earth's surface.

Now the intensity at the earth's surface does increase with magnetic latitude up to a certain latitude and then fails to increase further with continued increase of latitude; but, the place where the increase stops is not 60° but 41°, where the vertical energy of entry is 6×10^9 volts. Thus, as has been emphasized by Millikan, if we are to associate the observed latitude effect with the kind of story I have cited, we must accept the conclusion that six times as much energy is lost by a ray in penetrating the atmosphere as would be lost were ionization the only cause of such loss.[6]

In order to provide for the extra loss of energy, and more particularly to provide for a situation in which the observed intensity increases with altitude even in equatorial regions, I was led, a few years ago to postulate that, in addition to the loss by ionization, there was another loss which was proportional to the energy of the primary ray itself and which was responsible for the production of secondary rays among which we may include groups of rays or what are now called showers. Expressed mathematically, if E_z is the energy, the loss of energy is traveling parallel to the distance designated by x is assumed to be governed by the equation

$$-\frac{dE_z}{dx} = \lambda E_z + \alpha, \qquad (1)$$

where λ is a constant and α is a constant representing the loss per unit of path by ionization.[7] This assumption provides

[6] Since this report was presented several important advances have been made in the field of cosmic-rays. Among them is a paper by M. S. Vallarta which lends support to the view that the critical latitude is determined by the magnetic field of the sun rather than by that of the earth. This would modify the conclusion cited above, and would modify the *details* of certain parts which follow. However, no attempt will be made to incorporate these modifications in the present report, which here stands as given.

[7] In all cases we refer to distances measured in what is called the homogeneous water equivalent atmosphere, which is to be thought of as our atmosphere compressed to the density of water.

for a condition in which even in equatorial regions, where the primary intensity is independent of altitude, we nevertheless have an increase of the secondary intensity with altitude [8]

FIG. 5.

on account of the increase of energy of the primary energy with altitude.[9]

About the same time that the law specified by equation (1) was suggested, the modern wave mechanical theories of the

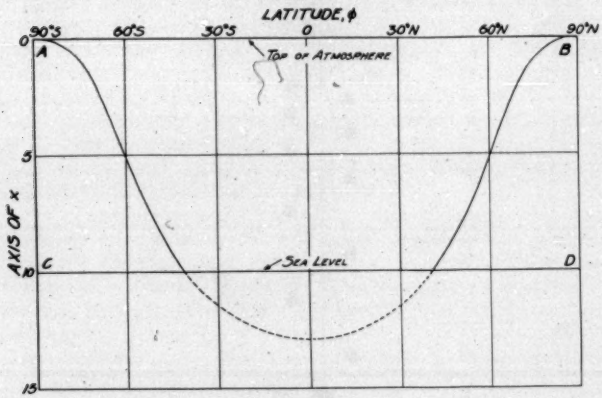
[8] At this stage of the lecture, the process of secondary production was illustrated by a moving picture cartoon. The primary particle P, entered the field of view at the top of the picture; and, as it descended it resulted in the appearance of secondaries whose copiousness of emission diminished with depth of penetration. Figure 5 shows a static picture from the cartoon.

[9] If we invoke conditions which correspond to large losses of primary energy in single acts, a straggling effect results for the primary. This straggling effect, even for equatorial regions, tends towards a true exponential law for the intensity as the losses in the individual acts tend towards complete loss of energy of rays concerned. However, straggling of this kind has never been developed to provide a very satisfactory story of the experimental phenomena; and, the views here developed are founded upon the existence of a range.

atom provided theoretical bases for the existence of the phenomenon assumed in that equation.

An understanding of the situation as regards the primaries and secondaries is enhanced by the contemplation of such a curve as is represented in Fig. 6. Here we have plotted downwards from the line AB, which represents the top of the homo-

FIG. 6.



geneous atmosphere, the distance of penetration of rays which can just succeed in getting through the earth's magnetic field at the corresponding latitude shown by the curve. The form of this curve depends upon the law which governs the loss of energy with distance traveled. As we have already remarked, it would cross the line CD representative of the earth's surface at a latitude of 60° in the case of electron rays were ionization representative of the only energy loss. The latitudes which lie between the points where the curve cuts the sea-level axis represent places where the minimum energy of penetration is greater than is necessary for complete penetration of the atmosphere and great enough, in fact, to provide for penetration to a distance below the surface of the earth such as is represented by the curve, with these distances, of course, expressed in terms of an absorbing substance the

equivalent of the material of the homogeneous water equivalent atmosphere.

The essential thing to be emphasized in connection with such a curve as Fig. 6 is that for all altitudes above the curve there would be no variation of primary intensity with altitude; and, any observed variation of intensity with altitude would there, on the theory proposed, be attributable to secondaries. In places below the curve, however, there would be a variation of primary intensity with altitude, the nature of that variation depending upon the energy distribution among the different primary rays entering. In these regions also we have, of course, the production of secondaries as well.

Now, in the detailed working out of the theory it became necessary to provide for what experiment reveals to be the case, that there is no very sharp change in the variation of intensity with altitude as we go from equatorial to higher latitudes. The provision for this fact enables one to determine the energy distribution in the incoming rays and the law of production of secondaries as a function of the energy. It also enables one to calculate possible situations as regards the relative numbers of primary and secondary rays. All of these are matters of considerable detail which are put out in the original publication and I must pass over them now.

The experimental analysis of the variation of intensity with altitude has led to the conclusion that this variation, which is complicated in itself, can be provided for by supposing that the radiation consists of a number of components in each of which the variation with altitude is simple and follows what the physicist calls an exponential law. In a fairly crude sense, but one sufficiently definite for practical purposes, it is possible to divide the radiation into two components, a so-called hard component, and a soft component, the former being about four times as penetrating as the latter. The theory which I have cited above applies to a single component and provides for the simple type of variation with altitude—the exponential law—to which I have referred. One may have a theory of this kind for the hard component and for the soft component; but, the nature of the considerations involved is such as to make the theory of greatest value in the case of the soft component which, as a matter of fact,

contributes by far the greater amount of the cosmic radiation in the atmosphere, in spite of the fact that at sea-level it is the hard component which dominates the situation.

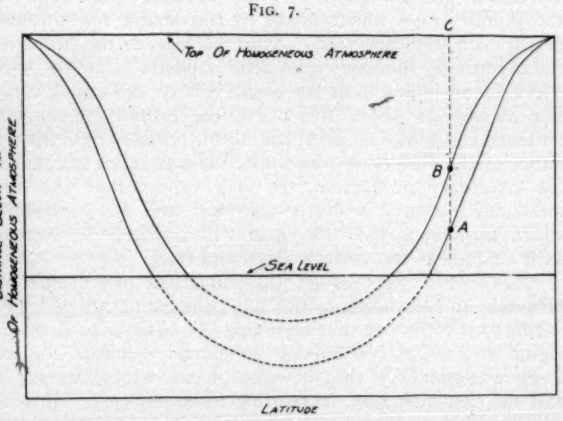
At this stage then various interesting considerations suggest themselves. Thus, for example, we may enquire whether the hard component need be of the charged corpuscular nature at all. We may enquire whether the directional effects are attributable to the hard component or to the soft component, or to both. We may enquire whether the latitude effect is a phenomenon only of the soft component, as it would be if the hard component were composed of uncharged rays, of photons, for example, or even of charged rays all of very high energy. It is of interest to examine some of these possibilities separately.

It is an experimental fact that the latitude effect increases with altitude, and since, at high altitudes, the soft component must dominate the situation it is obvious that the latitude effect of the soft component is representative of that effect which is to be found at high altitudes. Unfortunately, high altitude data upon the latitude effect are very meager and to some extent contradictory. However, information on the matter is accumulating, and at the Bartol Foundation, investigations to which I shall presently refer are in progress concerning it. A knowledge of its magnitude is of most profound importance, because, in a theory of the kind I have sketched it forms the most definite guide in crystalizing those details of the assumptions which enter into the theory as regards the law of production of secondaries as a function of the energy of the primaries. With the data at present available for determining the constants, it appears that it is possible to provide for a latitude effect for the soft component equal to about ten times that observed. Since the hard component at the earth's surface is about ten times the intensity of the soft component, if the hard component has no latitude effect it will serve to iron out the net latitude effect to the value observed.

The story of the east-west asymmetry is bound up closely with the matters under consideration. The meaning of this asymmetry can be best understood by appealing to curves similar to those of Fig. 6, but drawn for inclined directions

instead of a vertical direction. Thus, let us consider the magnetic equator and draw a line in the equatorial plane at an angle of 45° west of the zenith. We may then enquire the minimum energy of entry for this direction and plot a point representing the vertical depth of penetration for that energy and for the angle specified. We may do the same thing for a line inclined 45° to the east and obtain another point. We may do a similar thing for all magnetic latitudes and obtain two curves such as are shown qualitatively in Fig. 7, the upper

FIG. 7.



one for the west and the lower one for the east in the case of positive rays. For simplicity we shall confine our discussion to charges of one sign. Now, the asymmetry is determined by rays which can come in from the west and not from the east. Consider such a point as A on the lower of the two curves and suppose that a ray, to penetrate the distance represented by AC, is 5×10^9 e.v. Then in regions below A no rays which entered with less than 5×10^9 e.v. are to be found, whether they have come from the west or from the east. But rays of energy above 5×10^9 e.v. can come through the earth's magnetic field from east or west. Hence, we may say that, for regions below the lower curve, all rays which can

reach that far in the atmosphere could come in from east or west and there will be no asymmetry in that region. As we ascend in altitude and pass through the point A to a point B, we encounter additional rays which have come in from the west with energies less than 5×10^9 e.v., and so can reach only to the point B; but, rays of this energy could not come in from the east so that we have an asymmetry in the east-west intensities at B. This asymmetry increases with altitude until we get to the upper curve, above which any further increase of primary asymmetry is prevented by the fact that the primary rays which would be responsible for it cannot get in even from the west. Thus, as regards the primaries, the asymmetry increases from zero at points below the lower curve to an upper limit for points above the upper curve. For all regions above this curve the primary asymmetry remains constant, as does the total primary intensity in either of the directions concerned. However, on account of the secondary production, we may expect that the total measured intensity in either direction, and the asymmetry which represents the difference, will continue to increase with altitude at the same proportional rate.

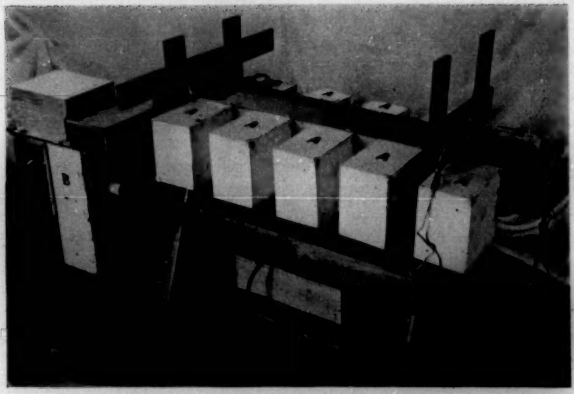
Now, when we consider the numerical magnitudes appropriate to the theory of the soft component which I have outlined, it turns out that assuming the equator to lie in the region above the two curves, we should calculate for sea-level an asymmetry, that is, ratio of east-west difference to half the east-west sum, amounting to 20 per cent. If, however, we assume the hard component to have no asymmetry and take the proportion between hard and soft component as given by former analyses, the expected asymmetry becomes ironed out to about 3 per cent. On the other hand, Dr. Johnson's measurements at the equator give an asymmetry ratio of 12 per cent. This could be accounted for by assuming an asymmetry for the hard component. However, before pinning oneself permanently to this view it is worth while observing that the ironing out of the asymmetry from 20 per cent. to 3 per cent. by the hard component results from the assumption that the vertical intensity of the hard component at sea-level is about 5 times that of the soft component. Now, the relative intensities of the hard and soft

components have been determined from data extending over wide regions in the atmosphere where intensities of magnitude, large compared with the surface intensities, have played a dominant rôle. Of course, if the cosmic radiation were composed absolutely of two pure components, a hard and a soft, observations taken anywhere in the atmosphere should lead to an estimation of their relative importance. If, however, the two-component concept is only an approximation, then in speaking of the contributions of those components to such phenomena as the latitude effect or the asymmetry effect at the earth's surface, it is important to determine the magnitudes of those components from observations taken relatively near the surface, and yet with sufficient accuracy to give the desired results. It is true that observations taken with ionization chambers at relatively low altitudes exist; but, their interpretation in terms of unidirectional rays is not as simple as might be desired.

Airplane Geiger-counter Measurements of the Vertical Intensity.—For the foregoing reasons, Dr. Danforth and I have modified, for airplane measurements, the apparatus which we sent up in the most recent National Geographic Society—U. S. Army Air Corps stratosphere flight; and, through the cooperation of General Oscar Westover, the head of the U. S. Army Air Corps, and Dr. Lyman J. Briggs. Director of the U. S. Bureau of Standards, we secured the services of Captain H. K. Baisley to fly this apparatus at altitudes extending from sea-level up to 24,000 feet.[10] These flights were made from the Philadelphia Navy Yard, through the courtesy of Commander W. W. Webster, who, I am happy to say, is with us this evening. In this apparatus we had the equivalent of twenty counter telescopes all pointed simultaneously in a vertical direction so that, even in the limited period possible in a single flight, we could obtain enough data on the vertical intensity to iron out the statistical fluctuations and secure satisfactory results. A picture of the counter telescope apparatus is shown in Fig. 8.

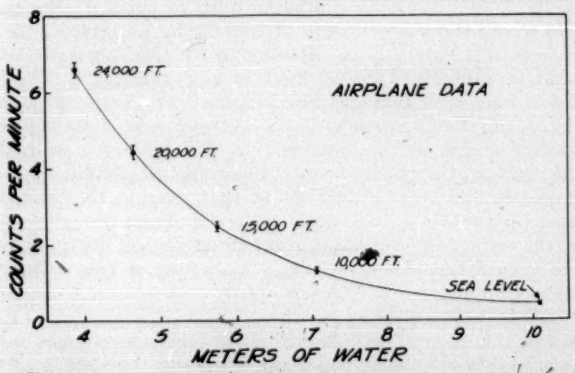
[10] It is a pleasure to acknowledge here the helpful cooperation extended by the Burgess Battery Co., who donated the dry cell batteries for this flight, and for former flights with this apparatus, into the stratosphere. I also wish to make similar acknowledgment to the R. C. A. Manufacturing Company, who donated the vacuum tubes for these flights.

FIG. 8.



The ten boxes marked *A*, one of which is invisible, represent ten pairs of counter telescopes, all pointing in the vertical direction. *B* is the recording unit. The details of these units were described in my report for last year. The main modification incorporated in the present instance is a heating arrangement to keep the clockwork mechanism warm under the temperature conditions encountered in the airplane,—conditions more severe than those encountered in the gondola in which the apparatus was housed in the stratosphere flights.

FIG. 9.

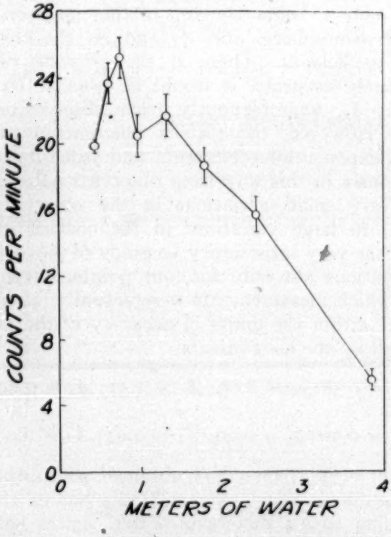


The points on the curve represent individual measurements and the vertical lines associated with them represent in the usual manner the statistical uncertainty resulting from limitation of the number of observations obtained.

The results are represented in Fig. 9. They correspond to observations at sea-level, 10,000 feet, 15,000 feet, 20,000 feet and 24,000 feet approximately.

It is of interest to see how these airplane measurements tie up with the observations made on the last National Geographic Society—U. S. Army Air Corps stratosphere

FIG. 10.



flight. Fig. 10, which I showed in my report last year and which had then just been obtained, shows the results which we had obtained for vertical intensity on that flight. The main object was to obtain observations at the highest altitudes; and, on account of the rapid descent of the balloon, it was not possible to secure very accurate data of the lower altitudes and, as a matter of fact, the batteries were thrown out as ballast at 15,000 feet, which corresponds in Fig. 10 to a depth of 6 meters below the top of the homogeneous water equivalent atmosphere. In spite of these considerations it

is interesting to observe that the airplane data and those from the former stratosphere flight fit together very well, and in a manner which will be more explicitly evident from what follows. Suppose that we should assign an intensity law of the form

$$I = A_1 e^{-\mu_1 x} + A_2 e^{-\mu_2 x},$$

where μ_1 and μ_2 are the two absorption coefficients, x the distance, in meters, below the top of the homogeneous water equivalent atmosphere, and A_1 and A_2 the corresponding intensity coefficients. Then, if the airplane observations were infinitely accurate, it would be possible to determine μ_1, μ_2, A_1, A_2, unambiguously from observations at four altitudes. However, the pitfalls inherent in attempts to determine exponential coefficients and intensity coefficients unambiguously in this way from observational data are well known. Very small variations in the observational data correspond to large variations in the coefficients.[11] Thus, in spite of the very satisfactory accuracy of the airplane data, the observations not only for four points, but for the five points at which measurements were actually taken, the data were fitted within the limits of accuracy of the experiments equally well by the assignments

$$\mu_1 = 0.58;\ \mu_2 = 0.00;\ A_1 = 1.57;\ A_2 = 0.0088$$

and

$$\mu_1 = 0.70;\ \mu_2 = 0.20;\ A_1 = 2.04;\ A_2 = 0.088.$$

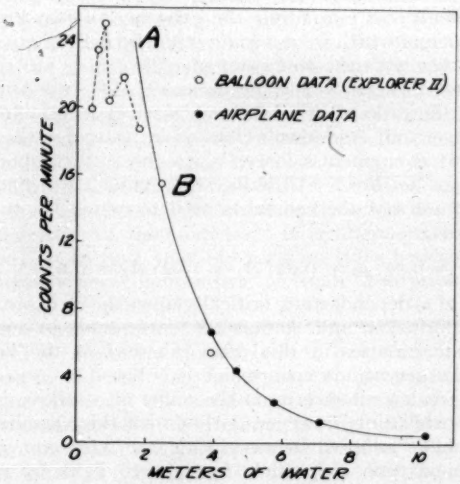
As a matter of fact, the curve obtained with either of these sets of constants, when extrapolated even to the altitude corresponding to 2.4 meters of water, agrees satisfactorily with the observation obtained for that point on the stratosphere flight already referred to.

Figure 11 shows between 10.3 meters of water depth (approximately sea-level) and the point A (2.0 meters of water depth), the curve obtained from the airplane flights, by use of the values $\mu_1 = 0.58$; $\mu_2 = 0.00$; $A_1 = 1.57$; $A_2 = 0.0088$, these values being obtained to correspond to the five observational points represented by black dots.

[11] W. F. G. Swann, JOUR. FRANK. INST., **209**, 151 (1930). L. D. Weld, *Phys. Rev.*, **40**, 713 (1932).

The portion of this curve to the left of the black dots is an extrapolation calculated on the basis of the foregoing constants. It will be observed that the airplane curve so extrapolated passes almost through the point B obtained in the stratosphere flight and corresponding to 2.4 meters of water. In fact, B falls off the curve by an amount which is within the limits of accuracy of observation. Moreover, even if the coefficients $\mu_1 = 0.70$; $\mu_2 = 0.20$; $A_1 = 2.04$;

FIG. 11.



$A_2 = 0.088$ were used, the airplane curve with its extrapolation would be judged to be as good a fit to the experimental points as is shown by the curve in Fig. 11. The departure of the observation from the extrapolated curve at the highest altitudes is, of course, only to be expected, and is bound up with considerations concerned with the effect of limitation of the atmosphere upon secondary production.

In view of the foregoing considerations it will be clear that, even with high accuracy in the experimental data, and even

with the assumption of two absorption coefficients, it is impracticable to determine those coefficients with any satisfactory degree of definiteness. If, however, from other considerations, we fix any one of the four magnitudes concerned, our data serve to determine the others unambiguously. If, indeed, we fix the ratio of the sea-level intensities of the two components, the story becomes unambiguously determined on the assumption, of course, of the existence of two absorption coefficients. If in line with the indications of recent researches, and in particular with researches described later in this report, we admit the existence of two kinds of particles, one of which we associate with the hard component, and the other with the soft component, we may use certain recent data of S. H. Neddermeyer and C. D. Anderson [12] to determine the ratio of the components at sea-level. In fact, Neddermeyer and Anderson's data yield 38/17 for the ratio of the hard component's intensity to the soft component's intensity at sea-level. Utilizing this value, we find the following values of the constants as determined by our airplane results:

$$\mu_1 = 0.59; \mu_2 = 0.02; A_1 = 1.64; A_2 = 0.010.$$

The value of μ_2 depends quite critically upon the ratio obtained from Neddermeyer and Anderson's data; and, in view of possible uncertainties in this ratio inherent in the limited number of observations upon which it is based, we must not place too great a reliance upon the value of μ_2 above given. The significant thing, however, is that with this visualization which we have adopted in associating the hard component with the new type of particle brought to light by recent investigations, our airplane results lead to an absorption coefficient for that hard component which is considerably less than has customarily been inferred from the empirical analysis of altitude intensity curves although the low value which we have found for μ_2 is actually in harmony with such empirical analysis within the limits of practical definiteness of such analysis, as has been demonstrated above by the fact that even up to the altitude corresponding to 2.4 meters of equivalent depth below the top of the atmosphere, we find

[12] S. H. Neddermeyer and C. D. Anderson, *Phys. Rev.*, **51**, 884 (1937).

that a satisfactory empirical analysis can be made with μ_2 as low as zero. The percentage uncertainty in μ_1 permitted by the empirical analysis, or even by the calculations based upon Neddermeyer and Anderson's data are less than is the case with μ_2, so that we may say that the value of μ_1 may be regarded as lying between 0.58 and 0.70. If we should limit ourselves to the values of μ_1 permitted by the Neddermeyer and Anderson data, taking into account its uncertainty, we should find μ_1 constrained to lie between the values 0.58 and 0.62.

Direct observations of the characteristics of the new type of particle have led to the conclusion that the absorption of these particles by matter is much less than might have been inferred by associating them with the hard component with a μ_2 such as it has been customary to assign formerly on the bases of empirical analysis of altitude intensity data. While our conclusions as to the magnitude of μ_2 have utilized the data of Neddermeyer and Anderson as regards the relative number of these particles, they have not utilized any elements from the experiments dealing directly with the absorption characteristics of the particles. It is, therefore, a matter of satisfaction to note that our airplane data had revealed independently the characteristic of small absorption for these hard component particles.

Quite apart from all matters dealing with the analysis of the altitude intensity curves, it is to be noted that the sea-level ratio of hard component to soft component intensity given as above by the Neddermeyer-Anderson data is about two to one instead of five to one, as cited earlier on the basis of pure empirical analysis of former results. The ratio two to one taken as a basis for the calculation of the asymmetry effect at the equator by utilization of the theory already referred to leads to a better harmonization of the experimental results than does the ratio five to one formerly assumed.

High Altitude Investigations.—In accordance with what has been stated above, it is clear that a knowledge of latitude variation and the change of latitude variation with altitude, and particularly the latitude variations at high altitudes are fundamental in determining the nature of those processes which are going on in the atmosphere and are responsible for what we observe. All the information comprised under

these heads would be provided by observations on the variation of intensity with altitude over a wide range of latitudes. Every stratosphere flight of the nature of those made by the National Geographic Society and by the Piccards and by the Russians, provide additional information and more such flights are contemplated. Hand in hand with them are going on a series of experiments using relatively small unmanned balloons, sometimes four or more together, for taking apparatus to high altitudes with suitable arrangements for automatic recording.

Investigations with unmanned balloons divide themselves into two categories. First we have those in which the phenomenon observed is the ionization produced by the cosmic-rays in an ionization chamber. Following this method extensive investigations are under way in the hands of R. A. Millikan and his collaborators. These have already given very important results and have recently confirmed the existence of a maximum in the cosmic-ray intensity at some altitude below the top of the homogeneous atmosphere. As will be recalled, we found such a maximum in the last stratosphere flight, and Regener found this maximum about the same time in Europe. In the apparatus used by Millikan, the records are made by photographic means and reliance has to be placed upon somebody finding the apparatus. However, in the experiments recently made in India about 60 per cent. of the apparatus sent up has been recovered. Again using the ionization chamber, a series of investigations are in progress by A. H. Compton and his collaborators. In these investigations the procedure is to record the observations while the balloon is in the air by means of radio reception from a radio transmitting apparatus carried by the balloon and operated by the cosmic-ray apparatus. This principle of receiving radio signals from an apparatus in the air has been in use by meteorologists for many years and the Harvard Meteorological Observatory has made considerable developments in that direction, so that the method is coming more and more extensively into use.

The alternative method of making observations is by the use of Geiger counters. The ionization chamber method has the disadvantage of giving an intensity which is averaged

in a rather complicated way for all directions while the Geiger counter method gives the intensity in a single direction. On the other hand, for given lengths of observation, the Geiger counter data are not as accurate as are the ionization chamber data, and this feature becomes more pronounced in the case of small unmanned balloons where the weight which can be carried is necessarily limited. It is here that the possibilities inherent in the manned flights have the advantage. It is true that if one is concerned with cosmic-ray investigations alone, the whole program of sending up many unmanned balloons with apparatus so as to secure a large number of results which in the aggregate would provide the accuracy desired could be carried out at far less expense than that for a single manned stratosphere flight. However, a manned stratosphere flight is usually carried out in the interests of a wide range of scientific projects; and, when such a flight is made, students of cosmic-rays should take the fullest advantage of it.

In view of the above considerations, investigations are under way at the Bartol Foundation for the determination of the variation of cosmic-ray intensity with altitude using Geiger counters and unmanned balloons. Last year, I described briefly an apparatus designed by Dr. T. H. Johnson for this purpose. This apparatus has since been perfected and preliminary flights have been made. It will be recalled that the features embodied in this apparatus are as follows: The high potentials necessary for operating the Geiger counters are supplied not by batteries which, in their commercially obtained forms, at any rate, are apt to be too heavy, but by a sort of electrostatic machine which is operated by gravity through the agency of a falling weight, falling, that is, in relation to the balloon system, that weight being, in fact, the apparatus itself. There is a radio device incorporated in the apparatus and every time a cosmic-ray passes through the cosmic-ray telescope a signal is transmitted to a land receiving station where it is recorded upon a moving strip of paper both photographically and by the principle of the telegraph recorder. It is necessary to transmit also the pressure so as to fix the altitude. This is done by means of a mercury barometer which makes electrical contacts at the various

pressures and by this means throws into an electrical circuit different resistances which control the pitch of a very low frequency vibration which is also recorded at the receiving station through radio transmission.[13]

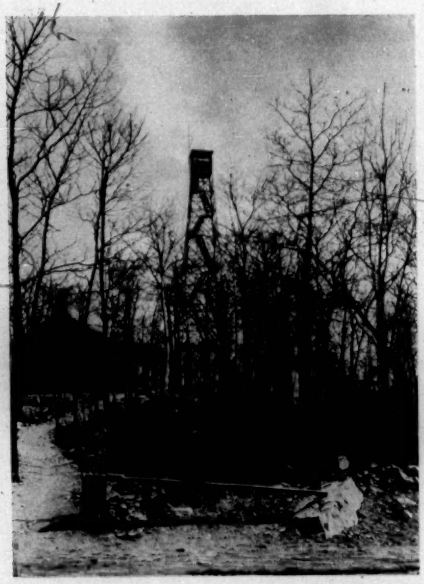
Figure 12 is a picture of an actual flight in operation. Fig.

FIG. 12.

[13] At this stage the apparatus was demonstrated. In order to realize a demonstration in a limited time, the apparatus was arranged to function with a single counter in place of the three used in actual measurements. A radioactive source placed near the ceiling served to simulate a situation in which there was an increase of measured intensity with altitude. The apparatus fastened to the ceiling was allowed to fall through a certain distance operating its electrostatic machine. During this period the rapidity of reception of the rays diminished and the rays themselves were received at the other end of the room by radio transmission; and for the purposes of demonstration were caused to operate a loud-speaker rather than a telegraph recorder.

13 is a picture of the antenna at the top of the Hopewell Fire Tower which, with other facilities, have been placed at the disposal of Dr. Johnson for this work by the Department of Forests and Waters of the Commonwealth of Pennsylvania, to whom I take this opportunity of expressing our thanks. Fig. 14 is a picture of the receiving station.

FIG. 13.



While the investigations are at present in a preliminary form, it is of interest to show Fig. 15, which gives the results of a recent flight. The legend on the slide gives its meaning. Vertically we have the relative number of rays received by the vertically arranged counters per unit of time. Horizontally we have depth in equivalent meters of water. The open circles represent the results obtained by Dr. Johnson's

FIG. 14.

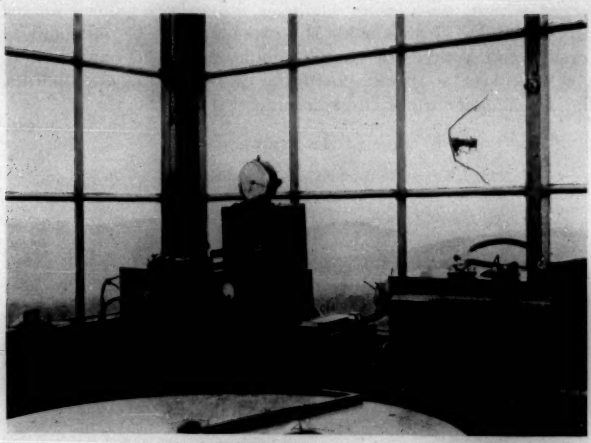
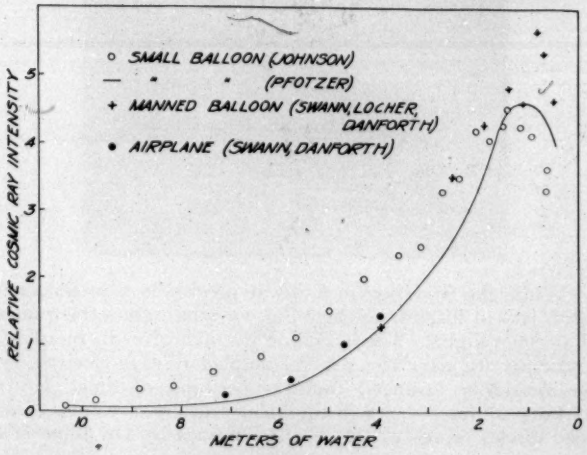


FIG. 15.


SMALL BALLOON (JOHNSON)
" " (PFOTZER)
MANNED BALLOON (SWANN, LOCHER, DANFORTH)
AIRPLANE (SWANN, DANFORTH)
RELATIVE COSMIC RAY INTENSITY
0
1
2
3
4
5
10
8
6
4
2
0
METERS OF WATER

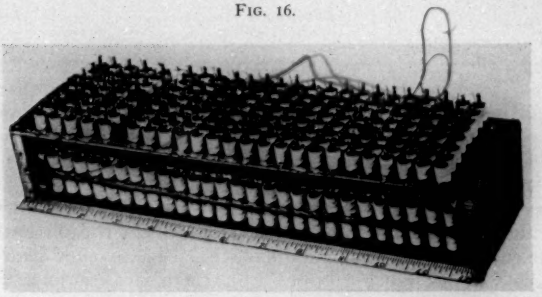
apparatus. The crosses represent the results obtained by the large apparatus which we sent up in the National Geographic U. S. Army Air Corps flight made in 1935. The smoothed curve represents results of an investigator, G. Pfotzer, in Europe. To these curves we have added the extra points represented by black dots, and corresponding to the recent airplane flights. The scales of all sets of observations are adjusted so as to give agreement at sea-level.

Pfotzer's results agree very well with ours over the whole range of our airplane and stratosphere measurements.

In order that we may have as many irons in the fire as possible and also in collaboration with some work which Professor Piccard is doing with unmanned balloons at the University of Minnesota, I have felt it worth while to give some attention recently to the design of a Geiger counter telescope apparatus for use in unmanned flights, and in which the records are made by photographic means and one relies upon finding the apparatus. In this apparatus the high potential for the Geiger counter assembly is provided by a battery. One of the most important developments which has rendered an apparatus of this type convenient and practicable has been the design of a battery of very light type by Mr. W. E. Ramsey. If one simply takes a battery of the ordinary type and shape and reduces the dimensions one encounters mechanical difficulties. These could be overcome without much trouble; but, there is something more important. The ratios of the amounts of the different chemical constituents involved in a battery and their disposition with regard to one another are important elements in the successful operation of the battery; and, these ratios do not remain at their proper values when the battery is simply reduced in size without alteration of its relative dimensions. The situation is somewhat analogous to that involved in engineering structures. One cannot duplicate structures in different overall sizes by simply altering all of the dimensions in proportion. Mr. Ramsey has made a study of the question of the relative disposition and amount of the chemicals involved in the battery and has succeeded in devising a situation in which it has been possible to produce a battery of 1000 volts, weighing no more than a pound and a half.

Moreover, this battery has the following features which are rather unusual for one of its type: (1) on open circuit it has shown a constancy of potential within 0.1 per cent. over a period of a week; (2) the battery will provide ten microamperes, that is, a hundred times as much as is necessary to operate the counter set, for a period of a week without diminution of more than 1 per cent.; (3) the temperature coefficient amounts to about a twentieth of one per cent. per degree centigrade; (4) a very important and unique feature of the battery is that by dehydrating it, by placing it in a dry atmosphere, it can be brought to a condition in which, while it is inoperative as regards giving any current, it is preserved from those internal chemical actions which limit

FIG. 16.

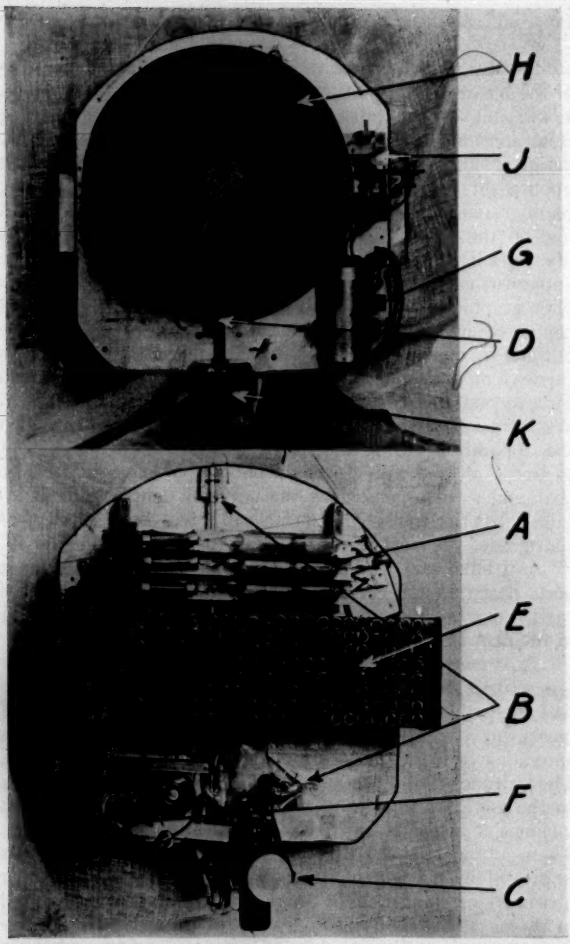


the life of a battery. It can be kept in this condition apparently indefinitely. Then when it is to be used, all that is necessary is to apply a medicine dropper with ammonium chloride solution to the cell and within a few seconds it is on the job, ready for service, with its full voltage and current carrying capacity.[14] A picture of a 1000 volt battery of the foregoing type is shown in Fig. 16.

[14] An experiment was shown demonstrating this feature. Then an experiment was shown in which an element of the battery was caused to send a current of 10 microamperes for a period of the remainder of the lecture without sensible alteration.

Since this report was presented, the development of this battery has been further advanced to a stage in which 1000 volts can be obtained with a weight of 0.75 lb., and a volume of 36 cubic inches.

FIG. 17.



The upper picture shows the recording mechanism and the lower picture the counter telescopes and barometer. *A* is the actual assembly of Geiger counters, *B* is the barometer which, by means of a reduction mechanism, in company with a light contained in *C*, throws an image upon a photographic film shown in the view from the other side at *D*.

E is the high potential battery and *F* is part of the vacuum tube assembly associated with the counter set. *G* is the electroscope which records upon photographic film wound on the light-tight drum *H* which is driven by a small electric motor *J*. *K* is the watch mechanism with recording film for the barometer.

The whole apparatus is enclosed in a copper housing which is not shown here.

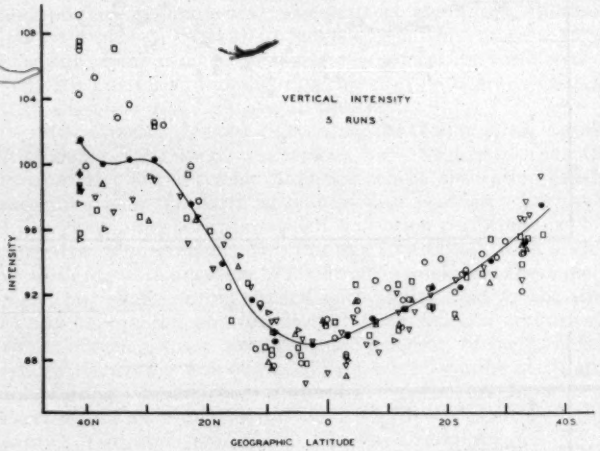
I will not spend time to describe in detail the operation of the recording mechanism of the Geiger counter apparatus. It will suffice to say that each Geiger counter impulse resulting from a cosmic-ray is caused to deflect the fiber of a suitably designed fiber-electroscope. The image of the fiber falls upon a slit behind which there is a rotating wheel carrying photographic film. When the fiber is still, it imprints a light line on the film as the wheel rotates. A deflection of the fiber lets light through producing a break in the line. The apparatus carries a barometer which likewise records upon a photographic film. The whole apparatus is enclosed in a copper sheath which keeps it at uniform temperature throughout and by means of suitably arranged pockets the apparatus carries a mixture of ice and water, the whole being surrounded by a second thin copper sheath and a heat insulating cover. We have calculated that with the heat insulation provided the apparatus, during the flight, will not lose enough heat to freeze all the water or gain enough to melt the ice, so that under these conditions the uniform temperature maintained by the inner copper inclosure will be zero degrees centigrade. A picture of the apparatus is shown in Fig. 17.

As I have said, the first of these pieces of apparatus has been designed for certain flights which Professor Piccard carried out in Minnesota; and, we hope to have one in the air in the near future.

Experimental Researches on the Latitude Effect.—Last year I described the apparatus which Dr. Johnson and Dr. Read had devised and installed upon a ship for the purpose of measuring the latitude effect over a wide range of latitudes extending from 41° geographic latitude North to 36° South. The latitude effect has been measured in a plane perpendicular to the meridian for the vertical direction and for directions inclined at angles of 45° to the east and to the west thereof. These observations have been continued with apparatus improved in matters of detail. The results of the former observations and those secured this year are incorporated in the next three slides. Fig. 18 is for the vertical intensity and one notices that the minimum intensity is found about 5° North of the geographic equator. As a matter of fact, it occurs at about 16° North of the geomagnetic equator. The

significance of this matter has already been pointed out in the publications by Drs. Johnson and Read,[15] and was referred to in my last report. The main effect of the additional results has been to enhance the accuracy of the final data; and, this enhancement continues as more observations are

FIG. 18.



secured. An interesting feature is shown by Figs. 19 and 20, which correspond respectively to the west and east directions. It will be observed that the latitude effect for the westerly rays is considerably less than that for the rays from the east. This result is an inevitable consequence of the theory of the matter according to which the asymmetry is determined by the action of the earth's magnetic field upon charged particle rays of preponderingly positive sign; but, these experiments are the first to demonstrate the reality of its existence.

The variation of the vertical intensity with latitude is something which depends upon the sum of the negative and

[15] T. H. Johnson, *Trans. Amer. Geophy. Union*, 1936, pages 176–178. T. H. Johnson and D. N. Read, *Phys. Rev.*, 51, 557 (1937).

FIG. 19.

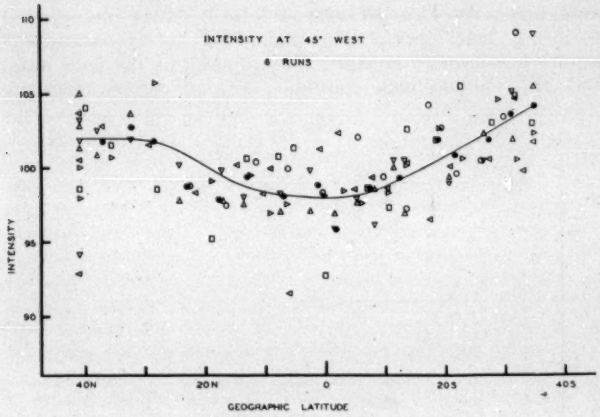
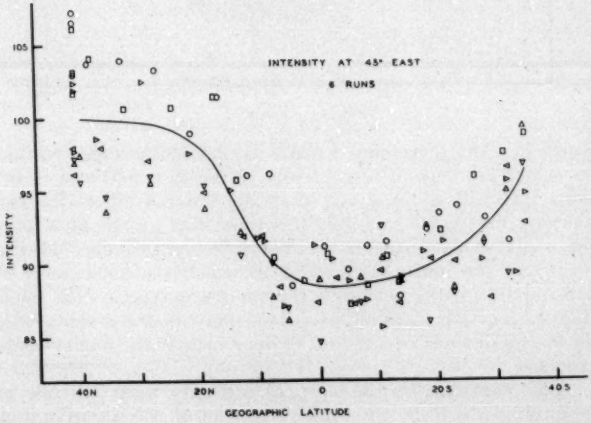

INTENSITY AT 45° WEST
6 RUNS
INTENSITY
110
105
100
95
90
40N
20N
0
20S
40S
GEOGRAPHIC LATITUDE

FIG. 20.


INTENSITY AT 45° EAST
6 RUNS
INTENSITY
105
100
95
90
85
40N
20N
0
20S
40S
GEOGRAPHIC LATITUDE

positive constituents in the cosmic radiation. The asymmetry and its variation with latitude is something which depends also upon the difference between the positive and negative constituents. With infinitely accurate observations, combined with a completely unambiguous theory, it would be possible to disentangle completely the story of the negative and positive components. As matters stand, Dr. Johnson has been able to draw the conclusion that not more than 30 per cent of the total corpuscular current can be composed of negative particles, and the experimental data are consistent with the view that they are all positive.

Miscellaneous Matters Concerning the Nature of the Cosmic Radiation.—Prominent authorities have suggested that the greater part of the cosmic radiation whose absorption can be measured near the earth is composed of protons. Last year I described an experiment which was being performed by Dr. and Mrs. Montgomery, Mr. Ramsey and myself with a view to deciding this question. I will not re-describe the experiment but shall content myself with saying that at the time of my report the conclusion had been reached tentatively to the effect that not more than ten per cent. of the radiation whose absorption was observed at sea-level can be attributed to protons. Since that time, the experiments have been carried to a more exhaustive finality with the result that that former tentative conclusion has been confirmed.[16] It is hoped to repeat this experiment at an altitude comparable with that of Pike's Peak, so as to ascertain more fully what the story may be there.

In connection with the theory of cosmic-ray phenomena to which I recently referred, it will be recalled that the picture was that of two components, a soft component and a hard component, and the story of the behavior of the former is traced rather completely in the theory. The question arises as to what is the physical nature of this component. Two kinds of charged particles have entered into consideration as representatives of primary cosmic-rays, particles of the electron type and heavier particles, such as protons, alpha particles, etc. The characteristics of these particles have

[16] C. G. Montgomery, D. D. Montgomery, W. E. Ramsey, and W. F. G. Swann, *Phys. Rev.*, **50**, 403 (1936).

been investigated from the purely theoretical standpoint by students of modern atomic theory; and, taking the conclusions reached by these investigators, Dr. Montgomery has applied them to the cosmic-ray problem, and particularly to the story of the soft component. He has reached the conclusion that electron-like rays are unsuitable as representatives of either the soft or the hard component primaries; but, he finds that, the theoretical characteristics of protons are such as to render them more readily to be representatives of the soft component of the radiation. This leaves open to some extent the nature of the hard component which, as far as these considerations go, might even be of a non-charged type.[17]

Cosmic-Ray Shower Phenomena.—When cosmic-rays pass through matter they occasionally result in the emission of large numbers of secondary rays composed of electrons, positrons, photons, and even heavy nuclear particles. The nature of these atomic bursts, or showers, as they are sometimes called, is of profound interest, and we have given much attention to them at the Bartol Research Foundation. In previous reports I have described several investigations on these matters. I have now to report upon a very interesting investigation carried out during the last year by Dr. and Mrs. Montgomery.[18]

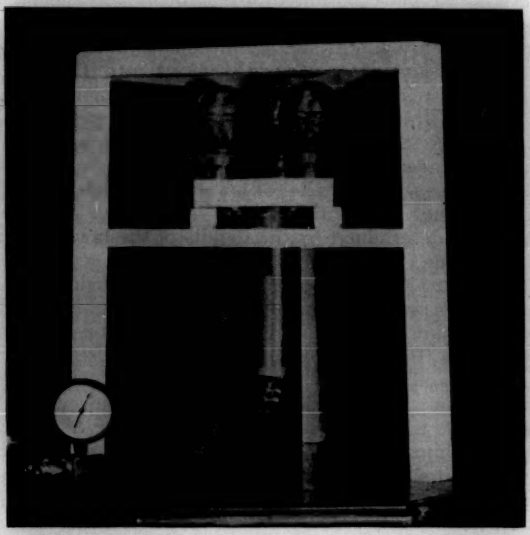
When such a phenomenon as that represented by cosmic-ray showers is under consideration one of the first things which interests the physicist is how the phenomenon is related to the element in which it is produced. In other words, he is interested in the answer to such a question as "How does the chance of production of a shower of some assigned size in a given thickness of material, as the result of a cosmic-ray passing through it, depend upon the atomic weight of the element composing the material?" As a matter of fact, the physicist usually speaks of the atomic number in place of the atomic weight, since that is a more fundamental quantity; but, the atomic number is roughly proportional to the atomic weight. The apparatus used by the Montgomerys comprised

[17] Since this report was presented, evidence for the existence of a new type of particle has been advanced by C. D. Anderson and by J. C. Street. This particle seems to have many of the features suitable for a representative of the hard component.

[18] C. G. Montgomery and D. D. Montgomery, *Phys. Rev.*, **50**, 490 (1936).

three small spheres containing gas at high pressure and provided with suitable electrodes and amplifying electrical devices to record the ionization produced in the three of them together when more than thirty ionizing rays went through them. Fig. 21 is a picture of the actual apparatus showing

FIG. 21.



the three spheres. Above the spheres was placed the material to be tested, and the experiment consisted in measuring the sizes of spurts of ionization produced in the three spheres acting together. The number of spurts of ionization obtained in a given time and lying between assigned limits of size was proportional to the probability that an atomic burst of the corresponding number of rays was produced in the specimen. By performing experiments with different specimens, the Montgomerys have shown that the probability of producing

a burst of any assigned size in a slab of material containing a fixed number of atoms is proportional to the square of the atomic number. Thus, for example, the probability of producing a shower in the case of lead is about fifty times that for the corresponding amount of aluminum. The verification of the foregoing law has a distinctive theoretical significance in connection with the question of how these showers are produced. In general, three mechanisms have been suggested: (1) The mechanism in which the original cosmic-ray becomes suddenly annihilated with the conversion of all of its mass, energy and atomic wordly goods into those of the shower which results; (2) A mechanism in which, while the energy comes from the primary particle, the process is one in which the first act is the production of a shower with few rays of high energy, whose particles in turn produce other smaller showers with particles of lower energy, which particles in turn continue the work, so that the shower grows to an ultimate size determined by the details of the laws governing the phenomena: (3) A mechanism in which the cosmic-ray acts more after the manner of an irritant, causing an atom to explode by processes analogous to or identical with those of induced radioactivity, in which case the energy of the shower comes from the atom. Now, while there are certain elements of ambiguity in the fundamental theoretical substructure of nuclear atomic physics which deals with these matters, there is a sufficiently definite sequence of principles to suggest almost inevitably that, if the phenomenon is of the type (1) it should depend upon the atomic number in the manner found by the Montgomerys; if it is of the type (2) it should follow a law definitely different from that; and, if it is of the type (3) it can only follow that law by a strange accident.

It may be of interest to combine the results of this recent investigation of the Montgomerys with the results of their former investigations which I have already reported and which have been published in detail [19] to the effect that, for any given material, the chance of producing a shower containing an assigned number of rays is inversely proportional to the cube of that number assigned. Taking into account

[19] C. G. Montgomery and D. D. Montgomery, *Phys. Rev.*, **48**, 786 (1935).

both of these results, we have that if R is the coefficient of dN in the expression for the number of showers produced from a given number of atoms of material in a given time and having numbers of rays between N and $N + dN$, then,

$$R = AZ^2/N^3$$

A further investigation by the Montgomerys concerns the way in which the production of these showers varies with the amount of matter which the primary rays producing them have traversed. They had already shown that the shower phenomena increased with altitude between sea-level and Pike's Peak much more rapidly than does the cosmic-ray intensity itself. On the other hand, they have shown that this situation does not continue to prevail as one descends to depths below sea-level. Time will not permit an exhaustive discussion of this question; but, it will serve to cite a tentative conclusion to which it leads to the effect that possibly the hard component and the soft component of the cosmic radiation are independently operative in the production of showers in different ways, suggesting, therefore, as has been sensed from other considerations, that they are of fundamentally different natures. While it is rather early to draw definite conclusions, it may be said that the results would be in harmony with a view according to which the increase of the soft component showers with altitude was more pronounced than the increase of the soft component itself, while the increase of the hard component showers with altitude followed the law of increase of the hard component itself.

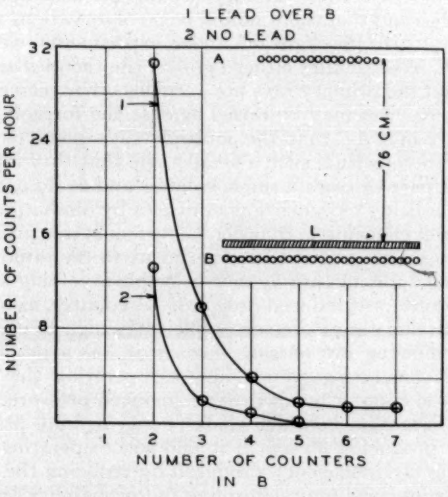
An Improved Apparatus for Measurements of Showers.—Perhaps at this stage it would be of interest to give a demonstration of the existence of these showers; and, for this purpose, I shall use an apparatus designed by Mr. W. E. Ramsey and which has had a wide range of applicability in researches upon shower phenomena. Time does not permit a detailed description of this apparatus further than to say that it is designed to have the following fundamental characteristics: First of all, there are two areas containing thin walled counters, one above the other, so that the combination defines, roughly at any rate, an angular direction in the sense that a telescope defines such a direction. There are twenty-

five counters in each layer, so that we have a total sensitive area of 500 square centimeters per unit. In an ordinary counter circuit the discharge of any two counters, one in one area and the other in the other, would give a record, and if more than two counters discharged in each area there would be a record of the same kind, so that one could not distinguish single rays from doubles, triples, or multiples. Mr. Ramsey has devised a system according to which the sizes of the impulses recorded are proportional to the numbers of counters discharged, so that the apparatus may be used for recording the number of singles, doubles, triples, and multiples passing through its telescopic angle. In actuality it is convenient to adjust the sensitivity so that an observable effect will be obtained when more than some previously assigned number of rays—let us say five—passes through the apparatus. The apparatus is now so arranged. We wish to show you the showers produced by this piece of lead. If we were on the roof we could do that very easily, but unfortunately in a room such as this there are all sorts of showers from the walls and ceiling; and, for all you know, there may be spurious phenomena, ghosts and demons, sent to embarrass Mr. Ramsey's demonstration. Now here are the showers from the room, which you may or may not accept my word for. We will chalk up the number which occur in five minutes. We will then place the piece of lead on top and hope that the number will be increased. Were we on the roof, these ghosts and demons would be absent and the effect of the lead would be more marked. It would be more marked because of the absence of the ghosts, and it would be more marked because of the greater intensity of the cosmic radiations in comparison with that in this room, where the radiations have to pass through the whole height of the building to reach the apparatus. While these numbers are being chalked up on the blackboard,[20] I will show Fig. 22, which tells the story of what does happen when the experiment is done out of doors. Vertically we have plotted the number of occasions in which, during an hour, we obtain through the apparatus a two-ray shower, a three-ray shower, a four-ray shower, and so on, as

[20] The experiment as carried out in the lecture room gave, over a period of 15 minutes, a 20 per cent. increase in showers in favor of the lead.

indicated on the horizontal axis. The lower curve is for the case without lead and the upper curve for that with lead. It will be seen that, for example, in the case of the three-ray showers, there is a factor of about five in favor of the lead. An interesting feature of the results shown by Fig. 22 is that we can obtain from them the number of showers of any given size resulting from an assigned number of cosmic-rays passing

FIG. 22.



through the specimen. The singles, in fact, give the numbers of cosmic-rays which can affect the counters, and the multiples give the story of the showers. Mr. Ramsey finds that on the average only eight per cent of the single rays which the counters record are accompanied by showers of more than two or more rays. Now, S. H. Neddermeyer, C. D. Anderson, P. M. S. Blackett, and others have shown that 75 per cent of all of the cosmic-rays which can operate counters are composed of charged particles which, if they are of electronic nature, must have energies of a thousand million volts or

more. Now, the modern wave mechanical theories of the production of these showers by cosmic-rays have led to the conclusion that in the case of electron rays, a 10^9 volt electron, in passing through a centimeter and a half of lead would result in the emission from the lead of four secondaries with energy greater than 10^7 e.v.; and, higher energy primaries would result in the emission of still more secondaries. These theories would thus lead us to expect that in this experiment every single electron primary would be accompanied by secondaries and that there should be no observations whatever of singles. In the light of these experiments we should, therefore, have to infer either (1) that the theories are wrong, or (2) that the primary rays are particles other than electrons.

One criticism may be raised against the foregoing experiment. It may be that the multiple rays predicted by the theories travel within such a small angle that they all pass for the most part through a single counter and so do not achieve the aim of being recognized as multiples by discharging different counter elements. In order to overcome this uncertainty, Mr. Ramsey has devised an experiment to the same end and depending upon an entirely new principle involving the use of Geiger counters at reduced pressure. A counter, as ordinarily used, contains gas at pressure sufficiently high to ensure that a single ionizing ray passing through it has a practical certainty of generating an ion and so operating the counter. Now, if the counter be operated at reduced pressure one may realize a situation in which there is only a finite probability of a ray producing an ion in it and so of operating it. By measuring the inefficiency produced by reducing the pressure in the counter one may determine the probability that a ray will produce an ion in passing a certain distance through the gas at atmospheric pressure. This principle of operating a counter at reduced pressure has been introduced by Dr. W. E. Danforth and Mr. W. E. Ramsey for determining the ionization per centimeter of path as cited in my last report and in a subsequent publication.[21]

Now using this principle, Mr. Ramsey and Dr. Danforth have arranged two layers of counters with pressure so low that the chance of a ray producing an ion in passing through

[21] W. E. Danforth and W. E. Ramsey, *Phys. Rev.*, **49**, 854 (1936).

one of them is only about seventeen per cent. The chance of it discharging two coincident counters is, therefore, only about seventeen per cent. of seventeen per cent., i.e. about 3 per cent. If a two ray shower should pass through the layers, it is easy to see that the chance of it operating both layers is approximately 4×3 per cent., whether the two rays go through different counters or through the same counter. The chance for a three-ray shower operating the counters is approximately 9×3 per cent., and so on. Now, suppose that we measure the number of impulses recorded by the two layers when exposed to the open sky, and find 100 in a certain time. Following the conclusions of Anderson, Blackett, etc., cited above, 75 of these are of energy greater than 10^9 e.v. If the two layers of counters are only three per cent. efficient, we shall get, from the hundred rays, only three counter impulses recorded when the apparatus is exposed to the sky. If now a sheet of lead 1.6 cms. thick is placed over the counters, if the primary rays are electrons, and if the theory to which I have referred applies, each of the 75 rays of energy greater than 10^9 e.v. should produce at least four secondaries; and it is easy to see that the efficiency of the otherwise inefficient counter set should be increased from three per cent. to about t[illegible] cent., so that it should record $75 \times 30/100 = 22$ [illegible], i.e. seven times as many as without the lead. Mr. Ramsey and Dr. Danforth find no such large increase due to the lead [22] and hence we must conclude either that the theory is wrong, or that the primary rays responsible for the most part in discharging the counter sets are not electrons. The actual increase in shower production produced by the lead in this experiment amounted to 50 per cent, and corresponds to a situation in which 6 per cent. of the recorded single rays produce showers. This result is in good agreement with that derived from the other experiment already cited.

Cloud Chamber Investigations.—A powerful method of investigating showers is that involving the use of the cloud expansion apparatus in which, as it will be recalled, one has a chamber containing moist air which can be cooled by expansion. If at the instant of expansion an ionizing ray passes

[22] W. E. Ramsey and W. E. Danforth, *Phys. Rev.*, **51**, 1105 (1937).

through the apparatus, water droplets condense upon the atoms in its path and render its track visible. Different kinds of rays are characterized by different kinds of tracks because the ionization per centimeter of path determines the broadness of the track and this ionization is characteristic of the rays. Moreover, some types of rays have energies sufficiently low to result in an appreciable number of those observed ending their paths within the observation chamber.

Dr. Locher, using the cloud expansion apparatus, has continued his researches upon the nature of the particles accompanying cosmic-ray bursts. The apparatus itself has gone through various stages of improvement which time will not permit me to describe. I must concentrate upon the general principles and the results. It is impossible to deal with more than one or two representative matters resulting from nearly a thousand photographs which Dr. Locher has taken and which are summarized in Table I. The object of

TABLE I.

Fractions of Pictures Showing Nuclear Tracks.

I. Recent Series.

Burst Material.	No. of Pictures.	Pictures with Nuclear Tracks.	Fraction Showing Nuclear Tracks.	
Lead	102	5	0.05	
Paraffin	79	8	0.10	
Nothing	73	2	0.03	
Aluminum	72	3	0.04	
Total:	326	18	Average = 0.055	Ratio: 3.66
Random	200	3	0.015	

II. Earlier Series.

Lead	50	4	0.08	
Paraffin	100	12	0.12	
Borax	35	2	0.06	
Aluminum	70	12	0.17	
Total:	255	30	Average = 0.117	Ratio: 3.36
Random	85	3	0.035	

III. Ratio for All Series.

Controlled	581	51	0.088	Ratio: 4.17
Random	285	6	0.021	

the table is to show, for various substances, the fraction of the atomic bursts which were associated with what are called nuclear tracks, that is to say, with particles of much heavier mass than the mass of an electron, particles comparable in mass with complete atoms. I will not pause to discuss the

FIG. 23.

significance of all that is contained in this table, but will concentrate upon simply one point concerned with Dr. Locher's research, a point which has been referred to before in my former report and concerning which Dr. Locher has published in the Physical Review.

I call attention to Fig. 23 which is a typical photograph—taken stereoscopically—of a cosmic-ray burst and in which

the single arrow points to a curious broad object which is to be the center of my remarks. Dr. Locher discovered these objects two or three years ago and much discussion has centered upon their nature, because they are so different from the straight, more or less thin, tracks which are normally associated with charged particles. Some have suggested that they are merely short alpha particle tracks which have been photographed after the diffusion of the ions which they produce. In order to test this matter, Dr. Locher has taken a large number of photographs at random—that is, photographs not associated with atomic bursts—and, he finds that the fraction of these photographs which show alpha particle tracks is only twenty-five per cent. of the fraction of the photographs of bursts which show these blobs. If, therefore, the blobs are alpha particles they muse be associated with atomic bursts. Now, it is reasonable to suppose that all of the atomic phenomena associated with a burst take place in a time very small compared with any time which could have significance in relation to the diffusion of ions such as would result in an apparent broadening of an otherwise fine track. Now, an examination of Fig. 23 shows that the electron tracks, two of which are indicated by double arrows, are quite sharp. If, therefore, the blob was created as part of the shower, it also must be regarded as a sharp representative of whatever it in actuality is. That it is in all probability a part of a shower is borne out by the other experiments to which I have referred and which have established the fact that the probability of obtaining blobs or any kind of wide form of track other than as part of a shower is small. There is just one loophole of escape from this conclusion, and that lies in the assumption that the shower is accompanied by the production of a state of induced radioactivity in some of the atoms of the shower producing material, resulting in a nuclear emission at a time sufficiently long after the initiation of the shower to permit of diffusion having played a rôle.

It is impossible in a single lecture to make even reference to many other phases of our work—to experiments which are in progress but have not yet reached the state where a report can be made—to many theoretical investigations in various stages of completion, and to some developments of a more

utilitarian nature which have evolved as side lines in our investigations of cosmic-rays and atomic physics. Physics today is in one of the most intense stages of activity of all time. Nature seems to have decided to open a new chapter in her story of the universe, and that chapter is the most exciting one that the man of science has so far read.

APPENDIX.

PUBLICATIONS OF THE BARTOL RESEARCH FOUNDATION FROM APRIL 15, 1936 TO APRIL 21, 1937.

The Absorption of Cosmic-Ray Showers in Lead—C. G. MONTGOMERY AND D. D. MONTGOMERY. *Phys. Rev.*, **49**, No. 10, pp. 705–711, May 15, 1936.

Energy Transmission by High Energy Electrons—W. F. G. SWANN. *Phys. Rev.*, **49**, No. 11, pp. 829–830, June 1, 1936.

The Specific Ionization of Cosmic-Ray Particles as Determined by Geiger-Mueller Counter Efficiency—W. E. DANFORTH AND W. E. RAMSEY. *Phys. Rev.*, **49**, No. 11, p. 854, June 1, 1936.

Neutrons and Other Heavy Particles in Cosmic Radiation of the Stratosphere—L. H. RUMBAUGH AND G. L. LOCHER. *Phys. Rev.*, **49**, No. 11, p. 855, June 1, 1936.

Biological Effects and Therapeutic Possibilities of Neutrons—G. L. LOCHER. *Amer. Jour. Roentgenology and Radium Therapy*, **36**, No. 1, pp. 1–13, July, 1936.

Report on the Work of the Bartol Research Foundation, 1934–35—W. F. G. SWANN. JOUR. FRANK. INST., **222**, No. 1, pp. 1–81, July, 1936.

The Forces Acting on High Energy Protons at Collision—A. BRAMLEY. JOUR. FRANK. INST., **222**, No. 2, pp. 141–148, August, 1936.

The Use of Geiger-Mueller Counters for Locating Radium and for Measuring Gamma-Ray Intensities—G. L. LOCHER AND J. L. WEATHERWAX. *Radiology*, **27**, No. 2, pp. 149–157, August, 1936.

A Search for Protons in the Primary Cosmic-Ray Beam—C. G. MONTGOMERY, D. D. MONTGOMERY, W. E. RAMSEY AND W. F. G. SWANN. *Phys. Rev.*, **50**, No. 5, pp. 403–407, September 1, 1936.

The Dependence of Burst Production Upon Atomic Number—C. G. MONTGOMERY AND D. D. MONTGOMERY. *Phys. Rev.*, **50**, No. 5, p. 490, September 1, 1936.

Über Koinzidenzen von Ultrastrahlungsstössen—C. G. MONTGOMERY AND D. D. MONTGOMERY. *Zeits. f. Phys.*, **102**, pp. 534–536, September 18, 1936.

Disintegration Experiments on the Separated Isotopes of Lithium—L. H. RUMBAUGH AND L. R. HAFSTAD. *Phys. Rev.*, **50**, No. 8, pp. 681–689, October 15, 1936.

Starting Potentials of Geiger-Mueller Counters—C. L. HAINES. *Rev. Sci. Inst.*, **7**, No. 11, pp. 411–413, November, 1936.

The Heavy Particle Component of the Cosmic Radiation—C. G. MONTGOMERY AND D. D. MONTGOMERY. *Phys. Rev.*, **50**, No. 9, pp. 975–976, November 15, 1936.

Report on the Work of the Bartol Research Foundation, 1935–36—W. F. G. SWANN. JOUR. FRANK. INST., 222, No. 6, pp. 647–714, December, 1936.

Wilson Cloud Machines for Portable Use—G. L. LOCHER. *Rev. Sci. Inst.*, 7, No. 12, pp. 471–478, December, 1936.

A Numerically Consistent Corpuscular Theory of Cosmic-Rays—W. F. G. SWANN. *Phys. Rev.*, 50, No. 12, pp. 1103–1119, December 15, 1936.

Cosmic-Ray Observations in the Stratosphere—W. F. G. SWANN, G. L. LOCHER, W. E. DANFORTH, C. G. MONTGOMERY AND D. D. MONTGOMERY. National Geographic Society Contributed Technical Papers, Stratosphere Series, No. 2, pp. 13–36, 1936.

The Solution of $\nabla^2\varphi - (1/c^2)\partial^2\varphi/\partial t^2 = -\alpha$—W. F. G. SWANN. *Amer. Phys. Teacher*, 5, No. 1, pp. 27–28, February, 1937.

The Nature of the Soft Component of the Cosmic Radiation—C. G. MONTGOMERY AND D. D. MONTGOMERY. *Phys. Rev.*, 51, No. 4, pp. 217–219, February 15, 1937.

Radio Transmission of Coincidence Counter Cosmic-Ray Measurements in the Stratosphere—T. H. JOHNSON. JOUR. FRANK. INST., 223, No. 3, pp. 339–354, March, 1937.

Unidirectional Cosmic-Ray Intensities and Their Variation with Latitude—T. H. JOHNSON. *Transactions of the Amer. Geophys. Union*, pp. 176–178, 1936; also reprinted in JOUR. FRANK. INST., 223, No. 3, pp. 379–385, March, 1937.

Geiger-Mueller Counter Measurements of Cosmic-Ray Intensities in the Stratosphere—W. F. G. SWANN, G. L. LOCHER AND W. E. DANFORTH. *Phys. Rev.*, 51, No. 6, pp. 389–390, March 15, 1937.

Unidirectional Measurements of the Cosmic-Ray Latitude Effect—T. H. JOHNSON AND D. N. READ. *Phys. Rev.*, 51, No. 7, pp. 557–564, April 1, 1937.

PAPERS PRESENTED AT VARIOUS MEETINGS BUT NOT PUBLISHED.

Presented before the American Physical Society.

Rochester Meeting, June 21–23, 1936.

Cosmic-Ray Disintegration in Light Elements—G. L. LOCHER.

The Production of Bursts of Cosmic-Ray Ionization from Various Materials—C. G. MONTGOMERY AND D. D. MONTGOMERY.

New York Meeting, October 29–31, 1936.

Geiger-Mueller Counters for Special Purposes—G. L. LOCHER.

A Possible Critical Latitude Phenomenon Limited to Altitudes Above Sea-Level—W. F. G. SWANN.

Atlantic City Meeting, December 28–30, 1936.

The Stopping of Fast Electrons—A. BRAMLEY.

Nuclear Disintegrations Accompanying Cosmic-Ray Showers—A. BRAMLEY.

Radio-Transmitted Coincidence Counter Measurements of Cosmic-Ray Intensities in the Stratosphere—T. H. JOHNSON.

Cosmic-Ray Bursts Photographed with a Cloud Machine Controlled by Noncollinear Counters—G. L. LOCHER.

Photoelectric Geiger-Mueller Counters for Visible and Ultraviolet Light—G. L. LOCHER.

Automatically Recorded Coincidence Counter Measurements of the Cosmic-Ray Latitude Effect—D. N. READ AND T. H. JOHNSON.

Durham, N. C. Meeting, February 19–20, 1937.

Range of High Speed Electrons—A. BRAMLEY.

Washington Meeting, April 29–May 1, 1937.

A Type of High Potential Battery which Combines Extreme Lightness with Long Shelf Life—W. E. RAMSEY.

Transmutation Processes of Li^6 and Li^7—L. H. RUMBAUGH, R. B. ROBERTS AND L. R. HAFSTAD.

Effect of Galactic Rotation upon the Intensity of Cosmic Radiation—W. F. G. SWANN.

The Electric Gage.—A very useful explanation, for informative as well as practical purposes, is that of the electric gage by C. M. HATHAWAY AND E. S. LEE in *Mechanical Engineering*, Vol. 59, No. 9. The paper is to be presented at a meeting of the American Society of Mechanical Engineers. An electric gage is a device for measuring linear dimensions or displacement by electricity and particularly for accurately measuring either small dimensions or small variations in larger dimensions. Displacements as small as 0.00001 in. or even 0.000001 in. can be read on an electric indicating instrument. Mechanical amplification ratio can be made as high as 10,000 or 100,000 or even higher if desired. It is fundamentally a device by which an electric current is controlled or modulated according to the relative position of two of its parts. This relationship between current and displacement can be brought about in several ways. Variations in resistance, capacitance, inductance, or wave form can be produced by variations in linear dimensions and these can be measured by variations in an electric current. The authors of the paper describe several methods of electric gaging which are interesting either because of historical background or value to a particularly interesting application. They are the capacitance, bridge, saturation and eddy current methods. Such instruments have been applied to strain measurement and have proved of great value to the mechanical engineer for analyses in loaded structures and machines. Factors contributing to the value of the strain gage for these uses are accuracy, small size, possibility of calibration on a testing machine before use, permanency of calibration, and the possibility of use with an oscillograph for obtaining permanent records of rapidly varying stresses.

R. H. O.

THE ENERGY HUMP IN CHEMISTRY. II.

BY

WILDER D. BANCROFT AND JAMES E. MAGOFFIN,

Cornell University.

HYDROGEN.

The hydrogen-hydrogen ion reaction is a paradoxical one. There is an energy hump in both directions and consequently the hydrogen electrode belongs theoretically in the class with the chlorate-chloride electrode. Actually it is so reversible and reproducible that electrochemists use it as a standard.

Molecular hydrogen does not reduce activated chlorate but does reduce potassium ferricyanide slowly. That means that the reaction potential of molecular hydrogen corresponds to a value of $E_h = +0.70$ volt. Since a hydrogen electrode in a neutral or slightly alkaline solution gives a value [1] close to $E_h = -0.4$ volt, the energy hump for molecular hydrogen to hydrogen ion in an approximately neutral solution is of the general order of 1.1 volts. For the reaction, hydrogen ion to hydrogen in acid solution, the energy hump is given by the maximum over-voltage say 0.7–1.0 volt. Swann [2] claims to get much larger values in glacial acetic acid; but we are only considering aqueous solutions at present.

The difference between the hydrogen-platinum electrode and the chlorate-platinum electrode is that, experimentally, platinum eliminates the energy hump for hydrogen and does not for chlorate. Osmic acid must be added in the case of chlorates. Platinized platinum also eliminates the energy hump for the change of hydrogen ion to hydrogen gas, whereas a mercury electrode does not. Consequently a hydrogen-platinum electrode is reversible, whereas a hydrogen-silver, hydrogen-copper or hydrogen-mercury electrode is not.

We have an independent check on the apparent chemical potential of molecular hydrogen. Beketoff [3] showed that

[1] Lorenz and Mohn, *Z. physik. Chem.*, **60**, 422 (1907).

[2] Swann, *Trans. Am. Electrochem. Soc.*, **58**, 179 (1930).

[3] Beketoff, *Compt. rend.* **48**, 442 (1859).

hydrogen gas would precipitate silver and mercury but not copper or lead from dilute solutions of salts of these metals. Increasing the gas pressure increased the effectiveness of the hydrogen on silver and mercury salts—as it should. There was some question as to the purity of the materials used by Beketoff; but fifteen years later Russell [4] established the fact that pure hydrogen reduces pure silver nitrate solutions slowly, but more rapidly the more concentrated the solution.

Since $Ag|AgNO_3$ is given as $E_h = +0.808$ volt, the value for molecular hydrogen must be less than that. We run into a, presumably temporary, snag with silver oxide which is said to be reduced by hydrogen [5] in the cold. Kohlschütter [6] has prepared silver sols by the action of molecular hydrogen at 50°–60° on saturated solutions of silver oxide. It looks as though the cathode potential [7] for $Ag_2O|Ag$ in tenth-normal sodium hydroxide is about $E_h = +0.4$ volt. Caustic soda precipitates silver oxide and Mr. Clack has found that the potential in a silver oxide solution is nearly $E_h = +0.6$ volt. This is not as high as the activated chlorate electrode; but there may be an activation of the chlorate by platinum or there may be a slight activation of hydrogen by silver or silver oxide.

Glaser [8] claims that hydrogen does not reduce dry silver oxide below 34°, that the resulting product is silver suboxide, Ag_4O and that the reduction to metallic silver starts at about 63°. On the other hand Lewis [9] denies the existence of silver suboxide. It is clear that our knowledge of facts is inadequate.

Gladstone and Tribe [10] found that platinum-hydrogen reduced both chlorate and nitrate while carbon-hydrogen reduced chlorate but not nitrate. Smale [11] did not get any

[4] Russell, *J. Chem. Soc.*, **27**, 3 (1874).

[5] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **1**, 328 (1922).

[6] Kohlschütter, *Z. Elektrochemie*, **14**, 53 (1908).

[7] Lewis, *Z. physik. Chem.*, **55**, 465 (1906); Luther and Pokorny, *Z. anorg. Chem.*, **57**, 290 (1908); Rollet, *Compt. rend.*, **186**, 748 (1928).

[8] Glaser, *Z. anorg. Chem.*, **36**, 9 (1903).

[9] Lewis, *J. Am. Chem. Soc.*, **28**, 139 (1906).

[10] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 31 (1878).

[11] Smale, *Z. physik. Chem.*, **14**, 588 (1891).

satisfactory measurements for the electromotive force of a carbon-hydrogen electrode; but assumed that, for theoretical reasons, the value must be the same as that for the platinum-hydrogen electrode. This cannot be far wrong, because of the reduction of chlorates by carbon-hydrogen. If Smale was right in his application of Ostwald's theoretical views, the failure to reduce nitrate must be due to an inadequate activation of nitrate by carbon. As this point has not hitherto been raised, it is not surprising that there are not yet any experiments bearing upon it.

The data on reduction by molecular hydrogen in acid and alkaline solutions are meagre and contradictory. People have been so interested in the catalytic action of platinum that they have failed to study the fundamentals. Jones [12] claimed that hydrogen reduced potassium permanganate to manganic oxide—not manganese dioxide—in acid, neutral or alkaline solutions. Wanklyn and Cooper [13] confirmed the fact of reduction; but did not determine the reduction products. In a more acid solution the manganic oxide would probably have been converted to manganous sulphate.[14] We know that hydrogen does not reduce chlorine in the dark and consequently the energy hump for molecular hydrogen in acid solution must lie between 1.43 (manganese dioxide) and 1.37 (chlorine) volts, say 1.4 volts. On this basis, molecular hydrogen should reduce lead peroxide in sulphuric acid. While it undoubtedly does do this, we have not found any record of it.

Wanklyn and Cooper said that molecular hydrogen does not reduce potassium ferricyanide either in neutral or alkaline solution. Cooke [15] made apparently more careful experiments and found that hydrogen does reduce neutral potassium ferricyanide. If hydrogen reduces alkaline ferricyanide, its potential in alkaline solution corresponds to about $E_h = +0.50$ volt. It is certainly less than $+0.59$ volt. We shall not be far wrong if we say that the energy hump for molecular hydrogen in alkaline solution corresponds at least to 1.20

[12] Jones, *J. Chem. Soc.*, **33**, 95 (1878).
[13] Wanklyn and Cooper, *Phil. Mag.*, (5) **30**, 431 (1890).
[14] Meyer and von Recklinghausen, *Ber.*, **29**, 2554 (1896).
[15] Cooke, *Chem. News*, **58**, 103 (1888).

volts = 0.5 + 0.7. It does not seem probable that the experimental error is sufficient to make the three values of 1.4, 1.1 and 1.2 identical. It is more likely that the energy hump varies somewhat with the pH.

We have already seen that rise of temperature and increase of concentration decrease the energy hump for sulphuric acid. Higher temperatures increase the reducing action of hydrogen. This is due in part to a change in free energy; but still more to the gradual elimination of the energy hump. Ipatiew [16] studied the effect of pressure and temperature on tenth-normal solutions of salts of some heavy metals, though his experiments were not well planned. With fifth-normal cupric acetate he got traces of cuprous oxide at 40° and 104 Atm. He got more cuprous oxide but the solution remained blue at 60° and 105 Atm., 72° and 113 Atm., and 90° and 58 Atm. This last solution was tenth-normal and was nearly completely precipitated.

Complete precipitation of cuprous oxide was obtained at 70°–90° and pressures round 125 Atm. Cuprous oxide mixed with metallic copper occurred at 97° and a pressure of something over a hundred atmospheres, while metallic copper with a possible trace of cuprous oxide was obtained at 92° and 350 Atm. Complete precipitation of metallic copper was obtained at 120° and about 120 Atm.

With rising temperature and pressure the cupric acetate is reduced to cuprous acetate which hydrolyzes to cuprous oxide and acetic acid. Finally, there is a complete reduction of cuprous oxide in presence of acetic acid. Ipatiew considers that there is an unspecified critical temperature below which no copper can be obtained; but his experiments do not show this and we know that it cannot be true. What he actually found was that at pressures of around 125 Atm. there is no precipitation of metallic copper below 100°. What he meant to say was that the reaction is much more sensitive to temperature differences than to pressure differences.

Experiments with N/10 copper sulphate differed from the preceding ones chiefly in the fact that with the strong acid there was no detectable precipitation of cuprous oxide under

[16] Ipatiew, *Ber.*, 42 2078 (1909).

the conditions of the experiments. There was no precipitation of copper at 20° or 60° and 500 Atm.; but there was a possible precipitate at 90° and 150 Atm. Complete precipitation of copper occurred at 160°–210° at pressures of about 120 Atm. and upwards. There were no experiments at temperatures between 100° and 160°. One experiment at 210° in presence of tenth-normal sulphuric acid seemed to give a slightly purer copper; but there is nothing to show that the apparent difference has any real significance.

Wright and Luff [17] found that cupric oxide dried at 130° showed signs of reduction by hydrogen at 85°, whereas cupric oxide obtained by ignition of copper nitrate started reducing at 175°. Glaser [18] reports a slight loss of weight at 150° of cupric oxide prepared from the nitrate and complete reduction at 173°, which agrees well with the observations of Wright and Luff. It would be a great help if some ingenious person would make electromotive force measurements on copper-copper sulphate over the range of temperatures covered by Ipatiew. It is only a question of twenty atmospheres at the outside.

The pressure experiments of Ipatiew on nickel salts call for a word of comment. The value for $Ni|NiSO_4$ is given in the textbooks as about $E_h = -0.250$ volt. On this basis activated hydrogen will not precipate metallic nickel from an aqueous solution. On the other hand, hydrogen in a solution of pH = 7 is about $E_h = -0.3$–4 volt. Consequently hydrogen should precipitate nickel from a nickel solution buffered at pH = 7. Neumann [19] tested solutions of nickel, chloride, acetate, sulphate and nitrate with platinum and hydrogen, getting a slight precipitate which he considered not to be metallic. Of course no attention was paid to the hydrogen ion concentration at that time and consequently these experiments must be repeated with modern precautions. Precipitation of nickel from a nickelous sulphate will tend to change the pH more than precipitation from an acetate solution.

[17] Wright and Luff, *J. Chem. Soc.*, 33, 1 (1878).
[18] Glaser, *Z. anorg. Chem.*, 36, 11 (1903).
[19] Neumann, *Z. physik. Chem.*, 14, 195 (1894).

Ipatiew obtained complete precipitation of nickel from tenth-normal nickel acetate at 200° and 174 Atm., incomplete precipitation from tenth-normal nickel sulphate at 188° and presumably 174 Atm., and complete precipitation at 207°. This does not prove anything because we do not know whether he could have obtained complete precipitation from nickel acetate at 188°. On the other hand he did not get complete precipitation of nickel from tenth-normal nickel chloride at either 200° or 240° at estimated pressures of 174 Atm.

REDUCTION AND OXIDATION POTENTIALS.

To determine the apparent reduction potentials of so-called irreversible systems, Conant [20] added the substance to be examined to an equimolecular mixture of a reversible reducing agent and its oxidized form in a voltaic cell and determined whether the voltage was changed thereby. If it were, then the reversible system was a stronger reducing agent at that concentration than the substance under examination. In this way Conant determined the "apparent reduction potentials" of a number of organic compounds.

Since the comparison is made in the presence of the metal electrode, this will introduce an error in case the substance to be examined is activated by the metal electrode. An extreme case is when hydrogen is the substance to be examined. An error of about 1.1 volts would be found for molecular hydrogen in this way. Of course, this case would never occur, because hydrogen forms a reversible electrode at platinum and does not need to be determined indirectly. We have shown, however, that there is an error of at least 0.4 volt with dimethylacrylic acid, because this substance is reduced by platinum-hydrogen and not by chromous chloride. What determines the ordinary stability of an organic compound is the position of the energy hump. As has been pointed out, platinum-hydrogen will reduce nitrates whereas carbon-hydrogen [21] apparently does not.

[20] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1047 (1923); Conant, *Chem. Reviews*, **3**, 1 (1926).

[21] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 310 (1878).

Another method of handling a somewhat similar case and one which is applicable to Conant's problem was developed by Foerster.[22] It is impossible to determine the true potential for ozone by measurement at a platinum electrode, because the platinum decomposed the ozone. In Foerster's laboratory, Oberer[23] showed that ozone will oxidize cobaltous sulphate to cobaltic sulphate in acid solution and consequently has a higher oxidizing potential. He determined $E_h > 1.76$ volts. Later Jahn[24] raised the probable value to $E_h > 1.81$ volts.

Bancroft and Murphy[25] have used Foerster's technique in their study of hydrogen peroxide solutions. It gives the results that one usually wants and is better to that extent than Conant's technique. On the other hand Foerster's technique does not give all the information that one may want and it should therefore be supplemented by Conant's technique. Conant's method shows whether the compound to be studied is activated by the metal. It gives results for dimethylacrylic acid and for nitrates which are not right, but which may be important. Nobody knows what results nitrates will give in the presence of iron. If Foerster's technique and Conant's technique give the same results, there is no activation of the substance under examination by the metal of the electrode. If there is a difference between the two methods, that difference is a measure of the activation by the metallic electrode. In other words, Conant's method does not necessarily give the results which he thought that it did; but it may be a valuable instrument of research when applied properly. Conversely, tests should be made on hydrogen peroxide solutions by Conant's method to determine what activation by different metals occur. Of course there may also be activation of the testing substances as we know occurs with hydrogen; but these effects will have to be studied one by one. The difficulty in the past has been that people did not really know what they were measuring.

[22] *Int. Kongress angew. Chem.*, 4, 447 (1903).
[23] Oberer, Dissertation, Zürich (1903).
[24] Jahn, *Z. anorg. Chem.*, 60, 292 (1908).
[25] Bancroft and Murphy, *J. Phys. Chem.*, 39, 377 (1935).

OXYGEN.

Oxygen, like hydrogen, has two energy humps. In acid solutions it will oxidize ferrous chloride to ferric chloride and consequently molecular oxygen corresponds to a value $E_h > + 0.90$ volt. Since we consider the true potential for oxygen in the gas cell at pH 1 to be about + 1.22 volts, the energy hump for molecular oxygen to hydroxyl ion (or oxygen ion) is about 0.3 volt. For the change from hyroxyl ion (or oxygen ion) to oxygen, the energy hump is measured by the over-voltage and consequently corresponds to about 0.6 volt. In alkaline solutions molecular oxygen oxidizes manganous hydroxide and sodium sulphite. It therefore corresponds to approximately $E_h = + 0.12$ volt. If the alkaline oxygen electrode is taken as about 0.48 volt, this means an energy hump of perhaps 0.36 volt, not very different from the energy hump in acid solution.

Lead peroxide is an interesting case. It gives a reproducible electrode and in acid solutions it has a value of $E_h = + 1.63$ volts; at least 0.4 volt higher than the reversible value for oxygen. Since it does not break down spontaneously into a lower oxide of lead and oxygen, there must be an energy hump relatively to the formation of oxygen. This means that activated oxygen is given off, and we know that there is a high over-voltage at a lead peroxide anode. The energy hump relatively to oxygen must be small, because sunlight sets free oxygen from lead peroxide. Another way of saying the same thing is that there is no energy hump in the change from tetravalent to bivalent lead; but there is an energy hump involved in the setting-free of gaseous oxygen. In alkaline solutions there is no evidence of any energy hump in passing from lead oxide to lead peroxide or in the opposite direction.

In acid solutions cobaltic sulphate and permanganic acid belong in the same general class as lead peroxide. If we consider an over-voltage of 0.5 volts on smooth platinum, ozone and cobaltic sulphate will give off oxygen at smooth platinum while permanganic acid will require platinized platinum.

Nobody seems to have studied the reactions of ozone systematically, taking into account the relative chemical potentials of the reacting substances. There are enough

data, however, so that we can make a good guess at some of the regularities which will appear when the proper measurements are made. Ozone is apparently instable under all conditions, though Luther [26] says that ozone will maintain it titer for weeks at a time when kept in contact with carefully purified sulphuric acid. He gives no figures and it is wiser to postulate no energy hump between ozone and oxygen, the rate of decomposition being very small under certain conditions.

When ozone decomposes without reacting with anything, the reaction is necessarily $2O_3 \rightarrow 3O_2$. When ozone reacts with a substance, Brodie [27] showed that two types of reaction were possible, one in which only one oxygen of the ozone reacted and another in which all three reacted. These may be written schematically: $O_3 + R \rightarrow RO + O_2$ and $O_3 + R \rightarrow RO_3$. Brodie thought that there were more types of reaction; but Riesenfeld [28] showed that the others were only mixtures of these two. Since ozonides can be formed in which the three oxygens of ozone add on to a substance, presumably simultaneously, Riesenfeld postulated, without any theoretical or experimental evidence, that ozonides were a preliminary stage in every reaction in which all three of the oxygen atoms in an ozone molecule react. He therefore wrote:

$$O_3 \rightarrow O_2 + [O]. \quad \text{Oxidation number} = 1.$$
$$O_3 \rightarrow [3O]. \quad \text{Oxidation number} = 3.$$

The square brackets indicate the oxygen atoms which react. We feel that this formulation is neither necessary nor right. We prefer to write:

$$O_3 \rightarrow O_2^* + [O]. \quad \text{Oxidation number} = 1 \text{ or } 3.$$
$$O_3 \rightarrow [3O]. \quad \text{Oxidation number} = 3.$$

The star indicates that the O_2 may pass temporarily through a more reactive stage than molecular oxygen and may or may not react with the substance in question, depending on its reducing power under the conditions of the experiment. It

[26] Luther, *Z. Elektrochemie*, **17**, 633 (1911).

[27] Brodie, *Phil. Trans.*, **162**, 435 (1872).

[28] Riesenfeld and Egidius, *Z. anorg. Chem.*, **85**, 217, (1911); Riesenfeld and Bencker, **98**, 167 (1916).

is immaterial for the argument what the intermediate stage is; it may be the -O.O- which Bancroft and Murphy [29] postulate for hydrogen peroxide, or it may be something else. If the intermediate stage does not react, the oxidation number will be one; if it does react, the oxidation number will be three. If the oxidation number is three the oxidation takes place in two steps and there is no formation of an ozonide at any time. The second equation is the one postulated as the general case by Riesenfeld, in which there is intermediate formation of an ozonide.

It is easy enough to imagine a system in which the oxidation number would be three but where there would be no intermediate formation of an ozonide. If we pass ozone into alkaline pyrogallol, all the ozone and all the oxygen will disappear. Consequently the oxidation number referred to ozone will be three. This case does not come up actually, because Brodie was careful to run blanks and to make corrections if necessary for oxidation due to molecular oxygen.

If we substitute for alkaline pyrogallol substances which are less and less powerful reducing agents, we shall reach a point at which there will be no reduction of molecular oxygen but there will be complete reduction of the intermediate stage, O_2^* as we have written it. The oxidation number will be three.

With weaker and weaker reducing agents, there will be less effective oxidation by the intermediate stage, and the apparent oxidation number will drop from three to one, at which point the intermediate stage, O_2^*, will change completely to molecular oxygen. If we exclude the formation of ozonides, we shall get oxidation numbers approaching one with the weaker reducing agents and approaching three with the stronger reducing agents. That is approximately what is found, though the evidence is not as clear cut as one would like.

Some of the substances giving oxidation numbers of one are: fuming sulphuric acid, lead sulphate, alkaline ferric oxide, alkaline chromic oxide, hydrogen peroxide, alkaline potassium iodate, manganous sulphate, halide acids, potas-

[29] Bancroft and Murphy, *J. Phys. Chem.*, **39**, 377 (1935).

sium iodide, ferrous sulphate, mercurous nitrate, and ammonia.

Potassium iodide gives an oxidation number of one in slightly acid, neutral, or slightly alkaline solutions. In more acid and especially in more concentrated solutions the oxidation number approaches three, because concentrated hydriodic acid is quite an effective reducing agent. In more strongly alkaline solutions the oxidation number goes up. This is apparently connected with the fact observed by Bancroft [30] that an alkaline iodine solution (hypoiodite?) is a fairly strong reducing agent. All these substances behave as they should, because none of them are effective reducing agents, with the exception of the alkaline hypoiodite which does give a high oxidation number.

Among the substances giving oxidation numbers approximating three are sodium sulphide, stannous chloride, sulphur dioxide gas, neutral sodium sulphite, neutral sodium thiosulphate, and strongly alkaline potassium iodide. These are all, quite definitely, reducing agents with the exception of the alkaline potassium iodide and that becomes normal as soon as oxidized to hypoiodite.

The one serious exception is alkaline sodium thiosulphate which gives a lower oxidation number than the neutral salt, though the alkaline solution must have stronger reducing powers than the neutral one. Alkaline thiosulphate is quite instable [31] and oxidizes readily in the air; but it is not clear how this helps. Somebody will have to make a special study of this case.

The only question remaining is whether Riesenfeld can be right in postulating the intermediate formation of an ozonide in every case in which an oxidation number of three is obtained. An ozonide of the formula $SO_2 \cdot O_3$ is quite out of the question; the oxidation of iodides and hydriodic acid must go through the hypoiodite stage; and strong reducing agents must give oxidation numbers of three. There is therefore no reason for adopting Riesenfeld's postulate.

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[30] Bancroft, *Z. physik. Chem.*, 10, 396 (1892).

[31] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 10, 494 (1930).

ENERGIES OF ACTIVATION.

Some forty years ago many physical chemists were trying in vain to prove that all reactions were ion reactions. Today the fashionable belief is that only activated molecules [32] react.

The effect of rising temperature is assumed to involve an increase in the number of activated or "hot" molecules. Catalysis can be treated in a similar formal way by postulating that the action of a catalyst is equivalent to changing the molecular distribution, increasing the percentage of "hot" molecules at constant temperature without changing the total energy of the system. Assuming for the moment that we have a gaseous catalyst for a gaseous system, the hypothetical distribution produced by the catalyst will cause the activated system to react rapidly with a number of substances with which the normal system will react infinitely, slowly, if at all. Consequently, we shall have two systems differing analytically only by the presence of the small amount of catalyst; but reacting at enormously different rates with certain substances.

From the formal point of view it is immaterial how this activation is brought about: whether the mean molecular weight of the gas remains constant; whether it varies because of a dissociation (into monatomic hydrogen); or whether there is a stoichiometric reaction between the catalyst and any of the constituents. Catalysis occurs whenever there is a sufficient increase in "hot" molecules, this being produced by an altered distribution though with no change in total energy. Hinshelwood [33] has defined catalysis as the operation of any mechanism which opens an alternative reaction path by which the same products can be produced.

In general, the influence of a foreign gas on a gaseous reaction is not large.[34] If we exclude cases in which stoichiometric compounds are formed and some photochemically

[32] Cf. Semenoff, "Chemical Kinetics and Chain Reactions," 8 (1935); Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 133, 152 (1933); Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," 259 (1927).

[33] Hinshelwood, *The School Science Review*, No. 31, 169 (1927).

[34] Hinshelwood, "Kinetics of Chemical Change in Homogeneous Systems," 231 (1933).

sensitized reactions, it is debatable whether we know any cases in which a dilute gas will cause any appreciable change in the molecular distribution. Activation by water vapor is usually classed under this head, but we hope to show later that this is probably not justifiable.

When we have selective adsorption by a solid, we get the equivalent of a two-dimensional gas in which there may perfectly well be an excessive amount of "hot" molecules. On this hypothesis a good catalyst gives the equivalent of a relatively large concentration of "hot" molecules while a poorer catalyst gives a lower concentration of reactive molecules. Familiar instances of this are the contact sulphuric acid process with platinum, vanadium oxide and iron oxide cata-

TABLE I.
Decomposition of Alcohol at 340°–350°.

Composition of Gas.			Composition of Gas.		
Catalyst.	Per Cent. C_2H_4	Per Cent. H_2.	Catalyst.	Per Cent. C_2H_4	Per Cent. H_2.
ThO_2.....	100.0	trace	MoO_3.....	23.0	77.0
Al_2O_3.....	98.5	1.5	Fe_2O_3.....	14.0	86.0
W_2O_3.....	98.5	1.5	V_2O_3.....	9.0	91.0
Cr_2O_3.....	91.0	9.0	ZnO.....	5.0	95.0
SiO_2.....	84.0	16.0	SnO.....	0.0	100.0
TiO_2.....	63.0	37.0	CdO.....	0.0	100.0
BeO.....	45.0	55.0	MnO.....	0.0	100.0
ZrO_2.....	45.0	55.0	MgO.....	0.0	100.0
UO_2.....	24.0	76.0	Cu.....	0.0	100.0

lysts. When equilibrium is reached in appreciable time, the same equilibrium is obtained with all catalysts but at different rates.

With specific adsorption and consequently widely different molecular distributions on the surfaces of the adsorbents there is nothing to prevent two different reactions taking place to relatively different extents on different adsorbents. The classical case of this is the behavior of alcohol as studied by Sabatier.[35] The two reactions are $C_2H_5OH = C_2H_4 + H_2O$ and $C_2H_5OH = CH_3CHO + H_2$. Sabatier's data are given in Table I. They do not represent equilibrium. In our

[35] Sabatier and Mailhe, *Ann. Chim. Phys.*, (8) **20**, 341 (1910).

present state of knowledge, these data should be identical for equilibrium; but nobody has shown this experimentally.

This formulation does not as yet enable us to predict why these oxides behave as they do either quantitatively or qualitatively. It has seemed to most people, including ourselves, that the activation of hydrogen was unquestionably due to the formation of small amounts of monatomic hydrogen. The reactions of activated hydrogen are the reactions of monatomic hydrogen so far as we have gone; it is customary to postulate monatomic hydrogen dissolved in platinum; and monatomic hydrogen is apparently the simplest way of accounting for the phenomena of nascent hydrogen and overvoltage. On the other hand, the heat of reaction of monatomic hydrogen to molecular hydrogen is very large and the heat of liquefaction of molecular hydrogen is relatively small. The heats of adsorption of hydrogen [36] by platinum and by charcoal are so large relatively to the heat of liquefaction that one must either postulate an almost infinitesimal amount of dissociation into monatomic hydrogen or devise some other form of activation.

It does not make any difference whether the substance to be adsorbed is vapor, liquid or solid so far as the general theory is concerned. Most people would probably prefer to speak of a state of strain in the case of adsorption of a solid rather than to say a change in the molecular distribution; but that is merely a matter of phraseology. As soon as the displacement in the right direction becomes large enough, we shall have a reaction. The catalysis of heated potassium chlorate by manganese dioxide [37] and of selenium β by Marc [38] come under this head. Years ago, Saunders [39] showed that quinoline catalyzed the conversion of amorphous to metallic selenium.

When changing from reactions in gases to reactions in solutions the same general principles should be applicable and we should expect to get possible rearrangements of molecular distribution in addition to effects due to solvation.

[36] McBain, "The Sorption of Gases and Vapours by Solids," 406, 421 (1932).
[37] Bancroft and Magoffin, *Trans. Faraday Soc.*
[38] Marc, *Z. anorg. Chem.*, 85, 65; Berger, 75 (1914).
[39] Saunders, *J. Phys. Chem.*, 4, 423 (1900).

We know that we get rearrangements of molecular distribution whenever we dissolve a substance in a dissociating or a polymerizing liquid and these changes do not necessarily involve solvation, although there may be solvation in many cases. Chlorination of benzene and toluene by chlorine in presence of ferric chloride and sulphur chloride involves compound formation and changed distribution.

Eyring and Daniells [40] attribute all variations in the rate of decomposition of nitrogen pentoxide in solution to hypothetical solvates. If the reaction goes more slowly than they think it should, they postulate relatively stable solvates. If the reaction goes more rapidly than they think it should, they postulate the existence of relatively instable solvates which decompose more rapidly than the unsolvated nitrogen pentoxide. While this may be true in this particular case, there is no evidence for it and it is a preposterous hypothesis when considered as a universal explanation. It is not adopted by others.

Moelwyn-Hughes [41] finds that certain reactions take place relatively slowly in carbon tetrachloride and the hydrocarbons, more rapidly in alcoholic solutions. "The hydrocarbons are to be regarded as relatively inert solvents, and alcohols as exerting a positive catalytic influence. It is not correct to regard the 'fast' solvents as normal and the 'slow' ones as deactivating."

Grimm, Ruf and Wolff [42] have studied the effect of solvents on the rate of formation of tetraethyl ammonium iodide, one of the reactions studied by Moelwyn-Hughes. They find that solvents with high dipole moments increase the reaction velocities very much. The converse of this is also true that in substances of high electrical symmetry—hydrocarbons—the reaction velocities are small.

Richardson and Soper [43] have carried these relations one step farther. "It was observed that the effect of changing from a non-polar to a polar solvent is to increase the speed of

[40] Eyring and Daniells, *J. Am. Chem. Soc.*, **52**, 1472, 1486 (1930).

[41] Moelwyn-Hughes, *J. Chem. Soc.*, **1932**, 230.

[42] Grimm, Ruf and Wolff, *Z. physik. Chem.*, 13B, 301 (1931).

[43] Richardson and Soper, *J. Chem. Soc.*, **1932**, 38; *Proc. Roy. Soc.*, 140A, 71 (1933).

reactions where the products are polar relatively to the reagents and to decrease the speed of reactions where the reagent tends to disrupt the critical complex into those substances for which the solvent has the greater affinity."

Soper and Williams [44] say that "for reaction velocity in solution the equation $R = PZe^{-E/RT}$ is proposed, where P is a probability factor which varies with temperature and is connected with the relative polar nature of reagents and products." In other words Soper believes that reactions in liquids are to be treated like reactions in gases, with suitable corrections for the displacement of the molecular distribution.

From this point of view there is nothing surprising in the rate of reaction being one million times [45] as great in one solvent as in another. Since the action of the solvent is selective, it is not surprising that the order of effectiveness of the solvents should vary with the nature of the reaction [46] and we know that it does.

The action of osmium tetroxide in activating potassium chlorate may be, and very likely is, due to the formation of a stoichiometric compound; but osmium tetroxide is present in the solution as a liquid with potential solvent action [47] and we must not ignore the possibility of its acting as a solvent. A more interesting possibility of the same sort is hydrogen-ion catalysis. Hydrogen ion may act as an apparent catalytic agent because it is an essential part [48] of the reaction: $H^{\cdot} + BrO_3' + H^{\cdot} + I' \rightarrow HBrO_2 + HIO$. In the sugar inversion there may be an instantaneous reaction with sugar as postulated by Jones and Lewis [49] $R + H^{\cdot} \rightarrow RH^{\cdot}$, which then reacts with water. Since hydrogen ion can act like a liquid in whatever form it may be present, there is a possibility that its catalytic action may come properly under the head of solvent catalysis. Hinshelwood [50] says: "Homogeneous catalysts are in the same phase as the reacting

[44] Soper and Williams, *Proc. Roy. Soc.*, 140A, 59 (1933).
[45] Von Halban, *Z. physik. Chem.*, 82, 341 (1913).
[46] Carrara, *Z. physik. Chem.*, 16, 735 (1895).
[47] Bancroft, *Science*, (2) 82, 388 (1935).
[48] Judson and Walker, *J. Chem. Soc.*, 73, 410 (1898).
[49] Jones and Lewis, *J. Chem. Soc.*, 117, 1120 (1920).
[50] Hinshelwood, *The School Science Review*, No. 31, 169 (1927).

substances. Their action may be regarded as a limiting case of the solvent effect, though so pronounced that the actual formation of intermediate compounds is not improbable. . . . The many-sided catalytic activities of the hydrion may well be connected with its unique structure, which permits it to form an endless variety of compounds."

In the last century there was a great deal of work done, much of it by H. Brereton Baker, to show that certain reactions in homogeneous or heterogeneous systems do not take place in the absence of water vapor, a typical and well-established case being that of ammonia and hydrogen chloride. It has usually been assumed as a matter of course that this is a case of vapor-phase catalysis.[51] If one feels sceptical about water vapor, and still more about benzene vapor, catalyzing the reaction between ammonia vapor and hydrogen chloride gas, we must consider it as a wall reaction or as a chain reaction starting at the wall.

In the old days such a concept was impossible because there could not be any water on the walls until the partial pressure reached nearly the saturation pressure of water. Nowadays we know that it is very difficult to remove the water from the walls and that some or all of the water vapor added or left in was on the walls. We also know that many reactions which were supposed to be homogeneous gas reactions are wall reactions to some extent.

In Hinshelwood's laboratory R. E. Burk [52] consulted with H. B. Baker and passed carefully-dried ammonia and hydrogen chloride into "a glass vessel which had been baked out at 200°–300° in a high vacuum. The glass had therefore no moisture which it could give up to the gas, but still held the film of adsorbed water which can only be stripped off by heating in a high vacuum almost to the point of fusion. An immediate reaction took place. No cloud of ammonium chloride was formed, i.e., there was no reaction in the gas; but a crystalline deposit spread over the surface of the vessel from the point where the gases entered. This showed that the reaction was a heterogeneous one catalyzed by the film

[51] Cf. however Hinshelwood, "Kinetics of Chemical Change in Homogeneous Systems," 244, 246 (1933).

[52] Hinshelwood, *The School Science Review*, No. 31, 169 (1927).

of adsorbed moisture on the glass. It explains moreover why the trace and no more of the moisture is needed. . . . The majority of the reactions in which the influence of moisture is marked are reactions in which a boundary surface plays a part."

There are other cases which seem to tie in. The reaction between phosgene and water, $COCl_2 + H_2O \rightarrow CO_2 + 2HCl$, is completely irreversible and yet there was a good deal of unofficial evidence during the World War that phosgene could be kept apparently indefinitely in contact with a sufficiently concentrated hydrochloric acid solution. If this is true it must mean that the reaction is a wall reaction poisoned by hydrochloric acid. Hinshelwood [53] says: "Many phenomena which look like the operation of homogeneous catalysis are really nothing of the kind. The characteristic reactions of atomic hydrogen appear only in the presence of water vapor, which might seem to show that water catalyzed the formation. Wood,[54] however, has shown definitely that the action of the water is to 'poison' the walls of the discharge tube, which otherwise cause an immediate catalytic recombination of the atoms."

CATALYSIS.

In 1891–92 Wilhelm Ostwald spent a good deal of time puzzling over the question whether to consider a catalytic agent in popular language as a lubricant or a siphon (*Potential-hub* was the word he actually used). He decided finally in favor of the lubrication concept: that the catalytic agent could accelerate a reaction which was actually taking place but could not initiate one. Ostwald developed this concept magnificently; and, pragmatically, he was right, though the recent developments have been along molecular-kinetic lines which he did not foresee.

We have now reached a point, nearly fifty years later, where it seems desirable to consider Ostwald's problem from another point of view. For practical purposes, molecular hydrogen in acid solution will not reduce in any reasonable

[53] Hinshelwood, "Kinetics of Chemical Change in Homogeneous Systems," 244 (1933).

[54] Wood, *Proc. Roy. Soc.*, 102A, 1 (1922).

time any reversible oxidizing agent unless the latter has an oxidizing potential of at least 0.4 volt on the hydrogen scale, and perhaps nearer 0.7 volt. For the moment we are not considering what would or would not happen in a million years. In presence of platinum black, reaction takes place as soon as the oxidizing potential exceeds zero on the hydrogen scale. Introduction of a catalytic agent has therefore been equivalent to a change of potential of at least a volt, since the value of hydrogen in neutral solution is about $E_h = -0.4$ volt. Since an electromotive force is a measure of some, not necessarily specified, difference of chemical potential, and since a catalytic agent cannot change the chemical potential, we must say that a catalytic agent may eliminate what is equivalent in this case to an electromotive force of at least one volt. This difference between the actual chemical potential and the apparent chemical potential is what we have called the energy hump. It could have been called the energy of inactivation but the other phrase is more descriptive.

Whether one determines the apparent chemical potential by the Foerster method or the Conant method, one is determining electrometrically the point at which the reaction velocity becomes zero or practically negligible. As was shown earlier in this paper, the reaction velocity is a function, among other things, of the molecular distribution. If one had suitable catalytic agents, one could vary the apparent chemical potential continuously from the value found when there is no catalytic agent to the value corresponding to the true chemical potential, as measured by the free energy. We can get the true chemical potential for hydrogen with platinum and for chlorate with osmium tetroxide and platinum. We can get a value for chlorate with pulverulent copper; but we do not yet know whether it is the same value that we get with osmium tetroxide or not. We can unquestionably get a special value for nitrate with iron but nobody has yet done it.

Since the effect of raising the temperature is similar in principle, by definition, to adding a catalyst, we should be able to get the results that we want by raising the temperature sufficiently. That has been done, though the results are not as accurate as one would like and are of course complicated to some extent by the change of both reacting substances

with changing temperature. Mellor [55] quotes from Berthelot that hydrogen starts reducing silver oxide at 0°, cupric oxide at 90°, lead oxide at 190°, and ferrous oxide at 305°. The exact figures are of no importance because they may vary considerably with the conditions of preparation of the oxides. The important thing is the order of the oxides and that is as it should be.

Since the electromotive force is an equilibrium phenomenon, the chemical potential as determined by it is independent of the molecular distribution as modified by a catalytic agent. Käb [56] claims that a hydrogen electrode poisoned by carbon monoxide may give an electromotive force 0.26 volt too noble. This is impossible if he was measuring the reaction, hydrogen gas to hydrogen ion; but it may be true if he was measuring some other reaction or if the electrode was not in equilibrium. Mercury and platinum electrodes with cysteine illustrate this point. Everybody appreciates that for the oxygen electrode. At 25° one never gets the true value for the oxyhydrogen-water gas cell because one is measuring the reduction of oxygen to hydrogen peroxide or the reduction of some oxide of platinum. In the true hydrogen electrode the electromotive force at equilibrium is independent of the molecular distribution postulated in the gas, in the electrode, or at the electrode. We can have any number of apparent chemical potentials but only one true chemical potential. No matter what apparent chemical potential one has, the difference between that and the true chemical potential as given by the free energy is a measure of the energy hump under those conditions of the experiment.

All the chemists except the physical chemists really believe that potassium chlorate and potassium perchlorate are stable substances at ordinary temperatures even when in the presence of manganese dioxide. The orthodox physical chemist believes that these compounds are decomposing all the time, but at an infinitely low rate. This belief is based upon the alleged properties of catalytic agents and on an extrapolation of the empirical equation for the change of reaction velocity

[55] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1, 329 (1922).

[56] Käb, *Z. physik. Chem.*, 115, 224 (1925).

with change of temperature. Since catalytic agents do not displace equilibrium, it seemed to follow that they could not start a reaction; in which case one must postulate that the reaction is going on all the time and is merely accelerated by the catalytic agent.

A siphon does not change the theoretical hydrostatic head at all and does not make water actually run up hill; but it makes a flow of water possible where no flow of water could occur before and it carries water over a very real energy hump. Consequently, if a catalytic agent can act like a siphon, it may initiate a reaction and it may act in a way which is equivalent to removing an energy hump. We have shown that energy humps do exist and that these can be eliminated in some cases by suitable catalytic agents.

It would help of course if one could show that certain reactions do not take place; but that is apparently impossible at present. It is easy enough to show that no measurable reaction takes place in any finite time that may be agreed upon; but the other fellow then says that he assumes that the reaction is taking place so slowly that one would not expect a detectable change under a million years. We reach a deadlock, because the experiment cannot be tested and because there is no theoretical proof as yet that the other man is wrong.

We had hoped to be able to do something with the petroleum deposits; but we have not the necessary facts. None of the petroleums are anywhere near theoretical equilibrium conditions and some of them are said to have been laid down approximately two hundred million years ago. It is immaterial whether this figure is right or not. The mathematical chemist can concede it and not be handicapped. If we assume, for the purpose of discussion, that the reaction velocity doubles for every ten degrees rise of temperature, the reaction velocity increases in round numbers approximately a millionfold for a rise of 200°, a billionfold for a rise of 300°, a trillionfold for a rise of 400°, and so on. Since there are approximately twenty-eight million seconds in a year, a change that would take place in about three seconds at any given temperature would take approximately one hundred million years at a temperature only five hundred degrees lower. If this extrapolation is permissible there seems to be nothing to be gained

from a study of the petroleums along these lines. There is no experimental evidence that will disprove the hypothesis of infinitesimally slow reactions in all apparently stable systems in which the free energy relations make a reaction possible.

There is another way of looking at the matter which is perhaps worth while. If we plot the Maxwell-Boltzmann distribution equation, as it is usually done,[57] with energy plotted along the abscissas and numbers of molecules plotted along the ordinates, we get a curve with a high maximum falling off rapidly in both directions to very small values. If we consider the portion of the curve extending out towards higher energies, there are two possibilities. Either the curve will meet the axis of abscissas at some point or it will approach the axis asymptotically. If the curve meets the axis of abscissas at any point, then reactions involving more energy of activity than corresponds to that point will not take place at all even in infinite time. If the curve never meets the axis of abscissas, we have the situation postulated by mathematical chemists; and a catalytic agent does not have to initiate a reaction because the reaction is always already under way.

For the apparently relatively simple case of free electrons in metals, the Maxwell-Boltzmann distribution has already been superseded by the Sommerfeld-Fermi distribution.

There is one corollary to the accepted view to which attention seems not to have been drawn. If the distribution curve extends practically to infinity in the direction of the higher energies, this means that in a sufficiently large volume of alcohol vapor, for instance, there will be at least one molecule having an energy corresponding to the energy which the vapor would have at a temperature of say 2000° or 3000°. We know that some chemists believe that there are molecules in a sufficiently large volume of alcohol vapor at room temperature which correspond to a temperature of 2000° or even 3000°. There may be many chemists who believe this, but we feel that such assumptions should be stated explicitly.

There is another point that should be considered. Important theoretical conclusions are being based on what is

[57] Loeb, "Kinetic Theory of Gases," 82 (1934); Daniels in Duggar, "Biological Effects of Radiation," 1, 255 (1936).

an extrapolation of a probability equation. What proof there is of the Maxwellian distribution of velocities [58] is not as yet adequate to justify the conclusions of the mathematical chemists. The argument from falling or rising temperature is based on an extrapolation of an empirical formula, which does not hold too well anyhow, the rate doubling to trebling for ten degrees rise of temperature. What people really mean is that if the formula held we should get reaction velocities with falling temperatures which could not be measured experimentally. Nobody questions this; but it is dangerous to conclude that a possible explanation is necessarily the right one. So long as we believed that a catalytic agent could not start a reaction and that the reactions were consequently going on, the argument from the Maxwell-Boltzmann distribution law and the argument from the temperature coefficients of the reaction velocities were welcome confirmations of what we knew to be true. Now that the major premise has gone by the board, the supporting arguments have practically no value at all.

Admitting that there is at present no crucial test in sight to enable us to differentiate between the opposing views of infinitely slow reactions and of no reactions at all, it may be well to show just how the new concept fits in with the facts that both sides admit.

We will take the case of potassium chlorate. We (meaning the senior author) believe that at room temperature there will be theoretically no decomposition of potassium chlorate in a million years or in any other arbitrarily selected period of time. If the temperature is raised, there will come a temperature at which decomposition will start. This temperature will be that at which the energy of excitation approximates the intersection of the molecular-distribution curve with the axis of abscissas. It will not necessarily be well-defined, like an inversion temperature, because there will undoubtedly be differences in molecular distribution which will cause the first decomposition to be very slow and consequently hard to detect. Manganese dioxide decreases the energy hump for potassium chlorate and consequently causes the reaction to take place at a lower temperature.

[58] Loeb, "Kinetic Theory of Gases," 113 (1934).

SUMMARY.

1. There are two energy humps for hydrogen. The one in the reaction from hydrogen to hydrogen gas varies with the nature of the cathode metal and is measured in each case by the over-voltage. The one from molecular hydrogen to hydrogen ion depends on the reducing power of molecular hydrogen. It apparently varies from about 1.1 volts in neutral solutions to about 1.2 volts in alkaline solution and to about 1.4 volts in acid solution. Platinized platinum removes both humps and consequently makes the hydrogen electrode a reversible one instead of being in the class with the chlorate-chloride electrode. The reason for the reaction between molecular hydrogen and silver oxide is not yet clear.

2. Since raising the temperature and increasing the concentration lower the energy hump, it is not surprising that Ipatiew was able to reduce copper and nickel salts with hydrogen at or above certain temperatures and certain pressures. It is probably not true, as Ipatiew assumed, that there is a critical temperature below which hydrogen will not reduce copper sulphate.

3. Foerster's method of determining apparent reduction potentials gives the true values but does not show the activating effect of the metals. Conant's method gives the apparent reduction potentials in presence of metals; but does not give the true values except when there is no activation by the metal. It is wiser to try both methods in any doubtful case.

4. From existing data the energy hump for oxygen is probably about 0.3 volt in acid solution and about 0.36 volt in alkaline solution.

5. We have shown that a concept similar to the one employed by Arrhenius to account for the temperature coefficients of reaction velocities can also be applied to all cases of contact catalysis at constant temperature. The important thing, however, is that we have shown that all cases of contact catalysis may be considered from a single view-point. Contact catalysis, solvent catalysis, hydrogen-ion catalysis, water-vapor catalysis, and the catalytic decomposition of manganese dioxide have hitherto been treated as five distinct cases. Whether hydrogen-ion catalysis is ever a solvent

catalysis is debatable; but it is a point of view which should be stimulating.

6. A catalytic agent may act like a siphon and not like a lubricant as postulated by Wilhelm Ostwald. If a catalyst acts like a siphon, it can and often does initiate a reaction. It will change the apparent reduction potential.

7. Potassium chlorate and potassium perchlorate are theoretically stable at room temperature. Molecular hydrogen will never reduce sodium sulphate or a solution of sodium sulphate at room temperature in the absence of a catalyzer.

8. Since an electromotive force is an equilibrium phenomenon, it is independent of any change of molecular distribution which does not change the chemical potential. Addition of a catalytic agent may increase the rate at which the electromotive force develops; but it cannot change the absolute value.

9. The apparent chemical potential is measured by means of reaction velocities and consequently can theoretically have any value between that in the presence of no catalyst and the true chemical potential as given by the free energy.

10. The physical-chemical fairyland, in which all reactions permitted by free-energy relations will always take place at least in fancy, owes its existence to a false assumption as to catalytic agents and to unlimited extrapolation of two approximation equations—the van't Hoff rule for temperature coefficients of reaction velocities and the Maxwell-Boltzmann distribution. This is not science.

11. Reactions may be divided broadly into three groups with no sharp dividing lines between the groups. (1) Many or all of the reactant molecules are in an activated state, in which case the reaction velocity is very great. Many of these are ion reactions. (2) Relatively few of the reactant molecules are in an activated state, in which case the reaction velocity is very small. These are the fashionable reactions to study at present. (3) None of the reactant molecules are in an activated state, in which case the reaction velocity under ordinary conditions is zero. These are the reactions which will be studied intensively in the next decade.

Redwood Byproducts.—(*Business Week*, September 4, 1937.) One of the largest lumber concerns in the west has accomplished a most spectacular development in the use of the bark of the redwood tree. On the standing tree, the tough, fibrous bark affords protection against fire and other encroachments of time. But from the beginning of redwood lumbering in 1852, it was necessary to strip the bark from the logs before taking them to the mills because no saw could be devised to cut the bark. Huge piles of the bark were left in the woods as waste material. Burning was difficult and expensive, and the slash fires necessary to dispose of the bark damaged young timber and seedlings essential to reforestation. The Pacific Lumber Co. built a bark-peeling plant at its mill in Scotia, north of San Francisco, together with shredders and driers based on textile industry practice. In processing the product, the bark is put into a shredder to be torn into tiny bits. Then it passes through a series of willowing and condensing machines which remove the dust and solid matter and clean the fibers, reducing them to a soft, fluffy red wool. The product is used as a heat insulator to insulate electric water heaters, in cold storage plants, home construction, air conditioning auxiliaries, and fur vaults. University athletic coaches also are finding the wool useful for running tracks. It is said to furnish a resilient filler under layers of cinders and clay.

R. H. O.

EQUIVALENT ELECTRONS AND THEIR SPECTROSCOPIC TERMS.

BY

C. L. B. SHUDEMAN,*

Institute for Advanced Study and Princeton University.

In 1927 Russell [1] gave a complete theory for the calculation of spectral terms arising from combinations of equivalent electrons, and Gibbs, Wilber and White,[2] who had solved the problem independently, published results in tabular form, obtained by them for s, p, d, and f electrons, which checked exactly with those of Russell. There is, however, a simple and more powerful method, quite interesting in itself and capable of yielding fairly easily the more complicated results for equivalent g, h and i electrons.

The relation of an electron to the atom of which it forms a part is most clearly described by Stoner's classification of electrons as belonging to certain shells and sub-shells, in which the orbits of the electrons are normally confined. The number n, which characterizes the shell, is the total quantum number, and the number l, which refers to the sub-shell of each shell, is the azimuthal quantum number:

Shell:	K $n=1$.	L $n=2$.		M $n=3$.			N $n=4$.				O $n=5$.					P $n=6$.
Sub-shell	$1s$ $l=0$	$2s$ $l=0$	$2p$ $l=1$	$3s$ $l=0$	$3p$ $l=1$	$3d$ $l=2$	$4s$ $l=0$	$4p$ $l=1$	$4d$ $l=2$	$4f$ $l=3$	$5s$ $l=0$	$5p$ $l=1$	$5d$ $l=2$	$5f$ $l=3$	$5g$ $l=4$	. . . .
Number of Electrons	2	2	6	2	6	10	2	6	10	14	2	6	10	14	18	. . . .

There are three other quantum numbers: the spin $s = \frac{1}{2}$ (in units of $h/2\pi$), and the magnetic quantum numbers $m_s = \pm \frac{1}{2}$, depending on the orientation of spin-axis, and m_l, which run over the integral values from l to $-l$, including zero.

* Professor of Physics, Florida Southern College, Lakeland.

[1] Russell, *Phys. Rev.*, **29**, p. 782 (1927).

[2] Gibbs, Wilber and White, *Phys. Rev.* **29**, p. 790 (1927).

Equivalent atoms are defined as those belonging to the same sub-shell or those having the same total quantum number n and the same azimuthal quantum number l. According to the Pauli exclusion principle no two electrons in the same atom may have all of their quantum numbers the same, which means that no two electrons in the same atom move in the same orbit. This limitation is already secured in the Stoner classification provided the two electrons belong to two different sub-shells. But for any two equivalent electrons there must be a difference in either the m_s or m_l or in both. If all the possible states of, say, an f-electron are written down, by pairing a value of m_s with a value of m_l:

m_s:	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
m_l:	3	2	1	0	−1	−2	−3	3	2	1	0	−1	−2	−3
States:	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*

there are found to be fourteen pairs which are different, which explains why there are always fourteen equivalent f-electrons in any complete sub-shell. A single f-electron may and must be in one of these states at any instant of time, and for a large number of similar atoms it may be supposed that every one of the states is equally represented, or "occupied" by the same number of electrons, this ensemble giving rise to the characterizations: $S = m_s = \frac{1}{2}$ and $L =$ maximum $m_l = 3$ for f-electrons, and yielding the spectroscopic term: ^2F, where the index 2 represents the "multiplicity," defined by $(2S + 1)$ of the corresponding energy-level, according to the accepted nomenclature by capital letters:

S	*P*	*D*	*F*	*G*	*H*	*I*	*K*	*L*	*M*
0	1	2	3	4	5	6	7	8	9

N	*O*	*Q*	*R*	*T*	*U*	*V*	*W*	*X*	*Y*	*Z*
10	11	12	13	14	15	16	17	18	19	20

where the numbers represent the maximum value of m_l for a "run" of integers from L to $-L$. Another simple case is where the f sub-shell is full, so that there are fourteen equivalent f-electrons, this configuration being denoted by f^{14}. Here each of the fourteen states is occupied by one electron, giving rise to only one combination, for which the summings yield:

$S = \Sigma m_s = 0$, and $L = \Sigma m_l = 0$, so that the resulting term is ^1S. For two f-electrons, f^2, one would write down all possible combinations of two different states: ab, ac, $\cdots$, bc, bd, $\cdots$, cd, ce, $\cdots$, mn, with the corresponding pairs m_s (= 1, 0 or -1) and m_l (= 5, 4, $\cdots$, -4, or -5) and from this aggregate determine the resulting terms. This is the method described in *Introduction to Atomic Spectra*, by H. E. White.

The plan of this paper deals with combinations obtained from electron states with spins of positive orientation, that is with the states a, b, $\cdots$, g only, in the case of f-electrons. The results will thus apply to that half of the electron states whose $m_s = \frac{1}{2}$ only. But by reasons of symmetry similar results hold for that half of the states for which $m_s = -\frac{1}{2}$. Then, by combining results appropriately in pairs, positive with negative, by "pseudo-term multiplication," to be defined below, and collecting parts, the desired terms can be written down. In other words, instead of computing, say, the terms arising from six equivalent f-electrons, f^6, directly from the fourteen states a, b, $\cdots$, n, the "pseudo-terms" of $f^1, f^2, \cdots, f^{14}$ are computed first of all, then the "pseudo-terms" of all desired pairs $f^p f^q$, where p and q run over the range 1, 2, $\cdots$, 14, are obtained by "pseudo-term multiplication," and from these it is easy to sort out the final complete terms, not only for f^6 but for all the various groups of f-electrons.

To illustrate: suppose the combinations of states belonging to g_+^3 are to be found and expressed by means of m_s and m_l:

m_s:	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
m_l:	4	3	2	1	0	-1	-2	-3	-4
State:	a	b	c	d	e	f	g	h	i

Write down all possible combinations of three different letters: abc, abd, $\cdots$, abi, acd, ace, $\cdots$, aci, ade, adf, $\cdots$, adi, aef, $\cdots$, aei, afg, afh, afi, agh agi, ahi. These are all the combinations which contain a. Proceed with another lot which contains b in each, but no a; and so on to the last lot ghi. These lots are easily seen to follow certain laws of ordering, when the m_l are written down instead of the letters, and can then be readily collected in consecutive "runs." For instance, in this case:

ab.	9	8	7	6	5	4	3					
ac.			7	6	5	4	3	2				
ad.					5	4	3	2	1			
ae.							3	2	1	0		
af.									1	0	−1	
ag.											−1	−2
ahi												−3
bc.	6	5	4	3	2	1						
bd.			4	3	2	1	0					
be.					2	1	0	−1				
bf.							0	−1	−2			
bg.									−2	−3		
bhi											−4	

and so on. When the resulting numbers are properly collected they will be found to form "runs": 9, 7, 6, 5, 4, two 3, and 1, which may be written compactly as: $(9_1.7_1 6_1 5_1 4_1 3_2.1_1.)_{3/2}$, where the subscript gives the number of times the "run" occurs, dots represent missing numbers, and the whole bracket is an aggregate of "pseudo-terms"; and the bracket subscript gives the $S = \Sigma m_s = \frac{3}{2}$. The reason for the designation "pseudo-term" is now apparent, for to have complete terms the bracket would also require the subscripts $\frac{1}{2}$, $-\frac{1}{2}$ and $-\frac{3}{2}$. There will be a similar bracket for the nine electrons with $m_s = -\frac{1}{2}$, for which the subscript will be $-\frac{3}{2}$, but the brackets for $m_s = \frac{1}{2}$ and $-\frac{1}{2}$ will have to come out of the aggregates $g_+^2 g_-^1$ and $g_+^1 g_-^2$, as will be shown immediately. The pseudo-terms for g_+^2 are: $(7_1.5_1.3_1.1_1.)_1$.

By combining the m_l (or L) values of two runs or pseudo-terms, in the manner of the Breit scheme, for $(4_1)(4_1)$ and also for $(4_1)(7_1)$,

	4	3	2	1	0	−1	−2	−3	−4
4	8	7	6	5	4	3	2	1	0
3	7	6	5	4	3	2	1	0	−1
2	6	5	4	3	2	1	0	−1	−2
1	5	4	3	2	1	0	−1	−2	−3
0	4	3	2	1	0	−1	−2	−3	−4
1	3	2	1	0	−1	−2	−3	−4	−5
2	2	1	0	−1	−2	−3	−4	−5	−6
3	1	0	−1	−2	−3	−4	−5	−6	−7
4	0	−1	−2	−3	−4	−5	−6	−7	−8
Runs:	0	1	2	3	4	5	6	7	8

	7	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7
4	11	10	9	8	7	6	5	4	3	2	1	0	−1	−2	−3
3	10	9	8	7	6	5	4	3	2	1	0	−1	−2	−3	−4
2	9	8	7	6	5	4	3	2	1	0	−1	−2	−3	−4	−5
1	8	7	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
0	7	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7
−1	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7	−8
−2	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7	−8	−9
−3	4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7	−8	−9	−10
−4	3	2	1	0	−1	−2	−3	−4	−5	−6	−7	−8	−9	−10	−11
Runs:							3	4	5	6	7	8	9	10	11

the runs indicated are obtained. These results show that in general this pseudo-term multiplication gives, for $p = q$,

$$(p_1)_u(q_1)_v = (p)^2_{u+v} = ((2p)_1(2p-1)_1\cdots 2_1 1_1 0_1)_{u+v},$$

and if $p > q$,

$$(p_1)_u(q_1)_v = ((p+q)_1(p+q-1)_1\cdots(p-q+1)_1(p-q)_1)_{u+v}$$

and

$$(p_r)_u(q_s)_v = rs((p+q)_1(p+q-1)_1\cdots(p-q)_1)_{u+v},$$

where the brackets have the proper subscripts to indicate the S.

Although in these combinings of combinations the m_s's and m_l's of two different runs or pseudo-terms are added, the word "multiplication" is justified by the fact that the two numbers of combinations multiply to give exactly the number of combinations of the resultant aggregate of pseudo-terms.

Thus the complete "product" $g_+{}^2g_-{}^1$, which contains $36 \times 9 = 324$ combinations, is

$$g_+{}^2g_-{}^1 : (4_1)_{-1/2}(7_1.5_1.3_1.1_1.)_1 = (4_1)_{-1/2}(7_1)_1 + (4_1)_{-1/2}(5_1)_1 + (4_1)_{-1/2}(3_1)_1 + (4_1)_{-1/2}(1_1)_1 = (11_1 10_1 9_1 8_1 7_1 6_1 5_1 4_1 3_1)_{1/2} + (9_1 8_1 7_1 6_1 5_1 4_1 3_1 2_1 1_1)_{1/2} + (7_1 6_1 5_1 4_1 3_1 2_1 1_1)_{1/2} + (5_1 4_1 3_1)_{1/2} = (11_1 10_1 9_2 8_2 7_3 6_3 5_4 4_4 3_4 2_2 1_2.)_{1/2}.$$

In practice this multiplication may be carried out as follows:

$$(4_1)(7_1.5_1.3_1.1_1.) = \begin{array}{r} 11\ldots\ldots\ldots\ldots 3 \\ 9\ldots\ldots\ldots\ldots 1 \\ 7\ldots\ldots\ldots\ldots 1 \\ 5\ldots\ldots\ldots 3 \\ \hline \text{Adding: } (11_1 10_1 9_2 8_2 7_3 6_3 5_4 4_4 3_4 2_2 1_2.)_{1/2} \end{array}$$

where the proper S-value is added as subscript to the bracket.

Returning to the case of three equivalent g-electrons: g^3, the spectroscopic terms are calculated as follows:

$$g^3 = g_+^3 + g_-^3 + g_+^2 g_-^1 + g_+^1 g_-^2.$$

Combinations: $816 = 84 + 84 + 324 + 324$

$$g^3 = (9_1.7_1 6_1 5_1 4_1 3_2.1_1.)_{3/2,\ -3/2} + (11_1 10_1 9_2 8_2 7_3 6_3 5_4 4_4 3_4 2_2 1_2.)_{1/2,\ -1/2}$$

$$= (9_1.7_1 6_1 5_1 4_1 3_2.1_1.)_{3/2,\ 1/2,\ -1/2,\ -3/2} + (11_1 10_1 9_1 8_2 7_2 6_2 5_3\ 4_3 3_2 2_2 1_1.)_{1/2,\ -1/2}$$

The last equation, which was obtained from the preceding one by shifting $(9_1.7_1 6_1 5_1 4_1 3_2.1_1.)_{1/2,\ -1/2}$ from the second bracket into the first bracket, is now expressed in complete terms, and may be written

Terms, g^3: $^4(9_1.7_1 6_1 5_1 4_1 3_2.1_1.)$, $^2(11_1 10_1 9_1 8_2 7_2 6_2 5_3 4_3 3_2 2_2 1_1.)$;

or, in capital letters, reversing the order of the terms inside the brackets,

Terms, g^3: $^4(.P.F_2GHIK.M)$, $^2(.P_1D_2F_2G_3H_3I_2K_2L_2MNO)$.

To review, and also tabulate results, the g_+ groups are first computed:

TABLE I.

Groups of g_+ Electrons.

P-T.	C.	G.	Resulting Pseudo-Terms.
1	9	g_+^1	$(4_1)_{1/2}$
4	36	g_+^2	$(7_1.5_1.3_1.1_1.)_1$
8	84	g_+^3	$(9_1.7_1 6_1 5_1 4_1 3_2.1_1.)_{3/2}$
12	126	g_+^4	$(10_1.8_1 7_1 6_2 5_1 4_2 3_1 2_2.0_1)_2$
12	126	g_+^5	$(10_1.8_1 7_1 6_2 5_1 4_2 3_1 2_2.0_1)_{5/2}$
8	84	g_+^6	$(9_1.7_1 6_1 5_1 4_1 3_2.1_1)_3$
4	36	g_+^7	$(7_1.5_1.3_1.1_1.)_{7/2}$
1	9	g_+^8	$(4_1)_4$
1	1	g_+^9	$(0_1)_{9/2}$

From these results, by pseudo-term multiplication, are calculated the pseudo-terms for all the various pairings (positive with negative groups) that will be needed:

TABLE II.
Pairings of g-Electrons.

P-T.	*C.*	Pairings.	Resulting Pseudo-Terms.
9	81	$g_+{}^1g_-{}^1$	$(8_1 7_1 6_1 5_1 4_1 3_1 2_1 1_1 0_1)_0$
28	324	$g_+{}^3g_-{}^1$	$(11_1 10_1 9_2 8_2 7_2 6_2 5_2 4_2 3_2 2_2 1_2)_{1/2}$
62	756	$g_+{}^3g_-{}^1$	$(13_1 12_1 11_2 10_2 9_2 8_2 7_2 6_2 5_2 4_2 3_2 2_2 1_2 0_1)_1$
90	1134	$g_+{}^4g_-{}^1$	$(14_1 13_1 12_2 11_2 10_2 9_2 8_2 7_2 6_1 5_1 4_1 3_2 2_2 1_2 0_2)_{3/2}$
104	1296	$g_+{}^3g_-{}^3$	$(14_1 13_1 12_2 11_2 10_2 9_2 8_1 0_7 1_6 0_1 2_5 1_1 4_1 3_2 2_1 0_1 1_4 0_4)_0$
226	3024	$g_+{}^3g_-{}^3$	$(16_1 15_1 14_2 13_4 12_7 11_8 10_{14} 9_{16} 8_{21} 7_{22} 6_{26} 5_{24} 4_{26} 3_{20} 2_{16} 1_{9} 0_8)_{1/2}$
328	4536	$g_+{}^4g_-{}^3$	$(17_1 16_1 15_2 14_4 13_8 12_{10} 11_{13} 10_{19} 9_{26} 8_{28} 7_{32} 6_{34} 5_{32} 4_{32} 3_{32} 2_{21} 1_{17} 0_8)_1$
500	7056	$g_+{}^3g_-{}^3$	$(18_1 17_1 16_2 15_5 14_8 13_{12} 12_{19} 11_{23} 10_{32} 9_{38} 8_{45} 7_{49} 6_{55} 5_{51} 4_{51} 3_{43} 2_{34} 1_{20} 0_{10})_0$
728	10584	$g_+{}^4g_-{}^3$	$(19_1 18_1 17_2 16_5 15_9 14_{12} 13_{21} 12_{27} 11_{38} 10_{46} 9_{58} 8_{64} 7_{74} 6_{74} 5_{71} 4_{69} 3_{62} 2_{48} 1_{32} 0_8)_{1/2}$
1070	15876	$g_+{}^4g_-{}^4$	$(20_1 19_1 18_2 17_4 16_{10} 15_{14} 14_{23} 13_{31} 12_{48} 11_{58} 10_{73} 9_{82} 8_{98} 7_{102} 6_{111} 5_{108} 4_{103} 3_{82} 2_{69} 1_{39} 0_{18})_0$

In these tables P-T gives the number of pseudo-terms; C the number of combinations; G, the group of electrons considered; and M, the multiplicity.

TABLE III.

Complete Terms Arising from g-Electrons.

C.	G.	M.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
18	g^1	2					1																
153	g^2	1	1	.	1	.	1	.	1	.	1												
		3	.	1	.	1	.	1	.	1													
816	g^3	2	.	1	2	2	3	3	2	2	2	1	1	1									
		4	.	1	.	2	1	1	1	.	1												
3060	g^4	1	3	.	5	2	6	3	6	3	5	2	3	1	2	.	1						
		3	.	4	3	6	5	7	5	6	4	4	2	2	1	1							
		5	1	.	2	1	2	1	2	1	1	.	1										
8568	g^5	2	3	5	10	11	15	14	15	13	13	10	9	6	5	3	2	1	1				
		4	1	4	6	8	9	9	9	8	8	6	4	3	2	1	1						
		6	1	.	2	1	2	1	2	1	1	.	1										
18564	g^6	1	7	3	13	11	19	13	21	14	17	12	13	7	9	4	4	2	2	.	1		
		3	1	13	13	23	21	28	23	26	20	20	14	13	8	7	3	3	1	1			
		5	2	3	8	7	10	9	10	8	8	5	5	3	2	1	1						
		7	.	1	.	2	1	1	1	1	.	1											
31824	g^7	2	5	15	24	31	37	39	40	39	36	32	27	22	17	13	9	6	4	2	1	1	
		4	2	13	16	25	25	30	27	28	23	22	16	14	9	7	4	3	1	1			
		6	1	3	5	6	7	7	7	6	5	4	3	2	1	1							
		8	.	1	.	1	.	1	.	1													
43758	g^8	1	10	7	24	20	34	28	37	28	34	24	26	17	18	10	10	5	5	2	2	.	1
		3	3	23	27	43	43	53	48	52	43	42	32	29	20	17	10	8	4	3	1	1	
		5	3	7	16	16	22	20	23	19	19	14	13	8	7	4	3	1	1				
		7	.	2	2	4	3	4	3	3	2	2	1	1									
		9				1	.																
48620	g^9	2	8	19	35	40	52	54	56	53	53	44	40	32	26	19	15	9	7	4	2	1	1
		4	6	16	24	34	38	40	42	39	35	32	26	20	16	11	7	5	3	1	1		
		6	3	3	9	8	12	10	12	9	9	6	6	3	3	1	1						
		8	.	1	1	1	1	1	1	1	1												
		10	1																				
$g^{10} = g^8$, $g^{11} = g^7$, $g^{12} = g^6$, $g^{13} = g^5$, $g^{14} = g^4$, $g^{15} = g^3$, $g^{16} = g^2$, $g^{17} = g^1$																							
1	g^{18}	1	1																				

TABLE IV.

Pseudo-Terms from Groups of h_+ Electrons.

P-T.	C.	G.	Resulting Pseudo-Terms.															
			15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
1	11	h_+^1											$(1)_{1/2}$					
5	55	h_+^2							(1	.	1	.	1	.	1	.	1	$.)_1$
13	165	h_+^3				(1	.	1	1	1	1	2	1	2	1	1	.	$1)_{3/2}$
24	330	h_+^4		(1	.	1	1	2	1	3	2	3	2	3	1	3	.	$1)_2$
32	462	h_+^5	(1	.	1	1	2	2	3	2	4	3	4	2	4	1	2	$.)_{5/2}$
32	462	h_+^6	(1	.	1	1	2	2	3	2	4	3	4	2	4	1	2	$.)_3$
24	330	h_+^7		(1	.	1	1	2	1	3	2	3	2	3	1	3	.	$1)_{7/2}$
13	165	h_+^8				(1	.	1	1	1	1	2	1	2	1	1	.	$1)_4$
5	55	h_+^9							(1	.	1	.	1	.	1	.	1	$.)_{9/2}$
1	11	h_+^{10}											$(1)_5$					
1	1	h_+^{11}																$(1)_{11/2}$

TABLE V.

Pseudo-Terms from Pairings of h-Electrons.

P-T. C.	P.	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
11 121	$h_+^1h_-^1$																					(1	1	1	1	1	1	1	1	1	1	$1)_0$
43 605	$h_+^2h_-^1$																	(1	1	2	2	3	3	4	4	5	5	5	3	3	1	$1)_{1/2}$
119 1815	$h_+^3h_-^1$														(1	1	2	3	4	5	7	8	10	11	12	11	12	10	9	7	5	$1)_1$
226 3630	$h_+^4h_-^1$												(1	1	2	3	5	6	9	11	14	16	19	19	22	21	21	18	17	11	8	$2)_{1/2}$
310 5082	$h_+^5h_-^1$											(1	1	2	3	5	7	10	12	16	19	23	24	28	28	29	27	25	20	17	9	$4)_2$
195 3025	$h_+^2h_-^2$													(1	1	3	3	6	6	10	10	15	15	19	17	20	16	18	12	13	5	$5)_0$
539 9075	$h_+^2h_-^2$									(1	1	3	4	7	9	14	17	24	28	35	38	45	45	50	47	48	40	37	24	18		$4)_{1/2}$

TABLE V.—*Continued.*

P-T. C.	P.	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
1034 18150	$h_+^4h_-^2$								(1	1	3	4	8	10	17	21	31	37	49	55	69	73	85	85	93	85	87	71	66	44	33	6)$_1$
1424 25410	$h_+^5h_-^2$							(1	1	3	4	8	11	18	23	34	42	56	65	82	90	106	110	121	118	128	108	103	80	66	35	17)$_{1/2}$
1525 27225	$h_+^3h_-^3$							(1	1	3	5	8	12	19	25	36	46	59	71	87	97	112	120	128	128	129	117	108	88	68	40	17)$_0$
2936 54450	$h_+^4h_-^3$					(1	1	3	5	9	13	22	30	44	58	78	96	123	143	171	191	215	225	241	237	236	216	197	157	125	71	28)$_{1/2}$
4036 76230	$h_+^5h_-^3$				(1	1	3	5	9	14	23	32	48	64	87	110	142	169	205	234	267	289	314	319	327	312	295	256	219	157	103	31)$_1$
5674 108900	$h_+^4h_-^4$			(1	1	3	5	10	14	25	35	53	71	100	126	167	201	249	287	338	368	412	428	451	441	438	394	361	287	225	129	54)$_0$
7804 152460	$h_+^5h_-^4$		(1	1	3	5	10	15	26	37	57	78	110	142	190	233	292	344	409	458	519	553	594	601	609	575	546	469	398	287	188	54)$_{1/2}$
10762 213444	$h_+^5h_-^5$	(1	1	3	5	10	16	27	39	61	85	121	159	214	268	340	408	490	562	645	703	769	799	827	811	791	719	644	520	398	236	90)$_0$

TABLE VI.

Complete Terms from Equivalent h-Electrons.

C.	*G.*	*M.*	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
22	h^1	2						1																									
231	h^2	1	1	.	1	.	1	.	1	.	1	.	1																				
		3	.	1	.	1	.	1	.	1	.	1																					
1540	h^3	2	.	1	2	2	3	4	3	3	3	2	2	2	1	1	1																
		4	1	.	1	1	2	1	2	1	1	1	1	.	1																		
7315	h^4	1	4	.	6	3	8	4	9	5	8	5	7	3	5	2	3	1	2	.	1												
		3	.	5	4	8	7	10	8	10	8	9	6	6	4	4	2	2	1	1													
		5	1	.	3	1	3	2	3	2	3	1	2	1	1	.	1																
26334	h^5	2	2	10	13	20	22	27	26	28	26	26	22	21	17	15	11	9	6	5	3	2	1	1									
		4	2	6	10	13	16	17	18	18	17	16	14	12	10	8	6	4	3	2	1	1											
		6	.	2	1	4	2	4	3	4	2	3	2	2	1	1	.	1															
74613	h^6	1	11	7	24	22	37	30	44	35	43	35	39	28	32	22	22	15	15	8	9	4	4	2	2	.	1						
		3	2	24	27	46	46	60	56	65	57	61	50	50	39	37	27	24	16	14	8	7	3	3	1	1							
		5	4	7	16	16	23	23	26	24	26	21	21	17	15	11	10	6	5	3	2	1	1										
		7	.	2	1	4	2	4	3	4	2	3	2	2	1	1	.	1															
170544	h^7	2	11	36	59	77	94	108	114	119	120	115	109	101	89	78	67	54	44	35	26	19	14	9	6	4	2	1	1				
		4	13	26	49	60	78	81	93	90	93	86	83	71	66	53	46	35	29	20	16	10	7	4	3	1	1						
		6	3	9	14	19	22	25	26	26	25	23	21	18	15	12	9	7	5	3	2	1	1										
		8	1	.	3	1	3	2	3	2	3	1	2	1	1	.	1																

TABLE VI.—*Continued.*

C.	G.	M.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
		1	23	26	68	68	105	99	126	114	132	114	123	101	104	82	80	59	57	39	36	23	21	12	11	5	5	2	.	1			
		3	14	68	91	139	153	187	190	209	198	204	183	177	152	140	113	100	76	64	46	37	24	19	11	8	4	3	1	1			
319770	h^8	5	15	27	55	63	85	87	101	96	102	91	90	76	71	56	50	37	31	21	17	10	8	4	3	1	1						
		7	1	8	10	16	16	20	19	21	18	18	15	14	10	9	6	5	3	2	1	1											
		9	1	.	1	1	2	1	2	1	1	1	1	.	1																		
		2	23	85	130	179	213	251	263	282	282	280	264	252	224	204	175	150	123	103	78	62	46	34	23	17	10	7	4	2	1	1	
		4	25	70	113	153	185	208	227	234	234	229	216	198	179	156	132	111	89	70	54	40	28	20	13	8	5	3	1	1			
497420	h^9	6	5	28	37	57	61	75	74	81	74	75	65	62	50	45	34	29	20	16	10	8	4	3	1	1							
		8	1	4	7	8	10	11	11	11	11	9	8	7	5	4	3	2	1	1													
		10	.	1	.	1	.	1	.	1	.	1																					
		1	36	48	111	122	175	173	216	202	226	205	216	184	187	153	146	116	107	78	72	49	43	28	24	13	12	6	5	2	2	.	1
		3	26	117	162	241	272	330	339	372	360	369	338	328	287	266	221	196	155	132	98	80	56	44	28	21	12	9	4	3	1	1	
646646	h^{10}	5	24	53	101	120	157	168	189	187	196	180	177	156	143	119	106	82	69	51	40	27	21	12	9	5	3	1	1				
		7	3	17	21	34	35	43	42	46	41	42	35	33	26	23	16	14	9	7	4	3	1	1	1								
		9	1	1	3	3	5	4	5	4	4	3	3	2	2	1	1																
		11						1																									
		2	36	107	173	233	283	325	353	370	376	371	357	335	307	275	241	207	173	142	114	88	68	50	36	25	17	11	7	4	2	1	1
		4	37	89	157	199	253	277	309	313	323	308	300	271	251	216	190	155	131	101	81	59	45	30	22	13	9	5	3	1	1		
		6	12	35	55	76	90	101	109	111	109	105	97	87	77	65	53	43	33	24	18	12	8	5	3	1	1						
705432	h^{11}	8	4	4	12	11	17	15	19	16	18	14	14	10	10	6	6	3	3	1	1												
		10	.	1	1	1	1	1	1	1	1	1	1																				
		12	1																														
			$h^{12} = h^{10}$, $h^{13} = h^9$, $h^{14} = h^8$, $h^{15} = h^7$, $h^{16} = h^6$, $h^{17} = h^6$, $h^{18} = h^4$, $h^{19} = h^3$, $h^{20} = h^2$, $h^{21} = h^1$																										
1	h^{22}	1	1																														

TABLE VII.

Pseudo-Terms from Groups of i-Electrons.

P-T.	*C.*	*G.*	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
1	13	i_+^1																$(1)_{1/2}$						
6	78	i_+^2										(	1	.	1	.	1	.	1	.	1	.	1	$.)_1$
18	286	i_+^3							(	1	.	1	1	1	2	1	2	2	2	1	2	.	1	$.)_{3/2}$
43	715	i_+^4				(1	.	1	1	2	1	3	2	4	3	4	3	5	2	4	2	3	.	$2)_2$
73	1287	i_+^5		(1	.	1	1	2	2	3	3	5	4	6	5	7	5	7	5	6	3	4	1	$2)_{5/2}$
94	1716	i_+^6	(1	.	1	1	2	2	4	3	5	5	7	6	9	6	9	7	8	5	7	2	4	$.)_3$
94	1716	i_+^7	(1	.	1	1	2	2	4	3	5	5	7	6	9	6	9	7	8	5	7	2	4	$.)_{7/2}$
73	1287	i_+^8		(1	.	1	1	2	2	3	3	5	4	6	5	7	5	7	5	6	3	4	1	$2)_4$
43	715	i_+^9				(1	.	1	1	2	1	3	2	4	3	4	3	5	2	4	2	3	.	$2)_{9/2}$
18	286	i_+^{10}						(	1	.	1	1	1	1	2	1	2	2	2	1	2	.	1	$.)_5$
6	78	i_+^{11}										(	1	.	1	.	1	.	1	.	1	.	1	$.)_{11/2}$
1	13	i_+^{12}																$(1)_6$						
1	1	i_+^{13}																						$(1)_{13/2}$

TABLE VIII.

Pseudo-Terms from Pairings of i-Electrons.

G.	42	41	40	39	38	37	36	35	34	33	32	31	30	29	28	27	26	25	24	23	22	21	20	19
$i_1^3i_{-1}$																								*
$i_1^3i_{-1}$																								
$i_1^4i_{-1}$																						(1)	1	2
$i_1^4i_{-1}$																			(1)	1	2	3	5	6
$i_1^5i_{-1}$																	(1)	1	2	3	5	7	10	13
$i_1^5i_{-1}$																(1)	1	2	3	5	7	11	14	19
$i_1^3i_{-3}$																					(1)	1	3	3
$i_1^4i_{-3}$																	(1)	1	3	4	7	9	14	17
$i_1^4i_{-3}$														(1)	1	3	4	8	10	17	21	32	39	54
$i_1^5i_{-3}$													(1)	1	3	4	8	11	18	24	36	46	64	79	103
$i_1^5i_{-3}$												(1)	1	3	4	8	11	19	25	38	49	69	86	114	136
$i_1^5i_{-3}$													(1)	1	3	5	8	12	19	25	36	48	63	79
$i_1^5i_{-3}$											(1)	1	3	5	9	13	22	30	45	61	84	108	143	175	220
$i_1^5i_{-3}$								(1)	1	3	5	9	14	23	33	50	69	97	128	171	216	276	337	412
$i_1^5i_{-3}$							(1)	1	3	5	9	14	24	34	52	73	103	137	186	236	305	377	465	554
$i_1^5i_{-4}$							(1)	1	3	5	10	14	25	35	55	75	108	142	195	245	319	391	487	575
$i_1^5i_{-4}$					(1)	1	3	5	10	15	26	38	60	84	122	165	228	295	389	488	617	748	912	1071
$i_1^6i_{-4}$				(1)	1	3	5	10	15	27	39	62	88	129	175	245	319	425	538	686	839	1035	1225	1459
$i_1^5i_{-5}$			(1)	1	3	5	10	16	27	41	65	93	137	189	264	350	467	599	768	952	1178	1416	1696	1976
$i_1^6i_{-5}$		(1)	1	3	5	10	16	28	42	67	97	144	200	282	376	507	655	847	1059	1323	1603	1939	2281	2673
$i_1^6i_{-6}$	(1)	1	3	5	10	16	29	43	69	101	151	211	301	403	548	714	931	1173	1480	1806	2205	2619	3097	3573

TABLE VIII.—*Continued.*

Pseudo-Terms from Pairings of i-Electrons.

18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0	G.
						(1	1	1	1	1	1	1	1	1	1	1	1	$1)_0$	$i_+{}^1i_-{}^1$
*	(1	1	2	2	3	3	4	4	5	5	6	6	6	4	4	2	2	$.)_{1/2}$	$i_+{}^3i_-{}^1$
3	4	5	7	8	10	12	14	15	17	16	17	16	15	13	12	8	6	$2)_1$	$i_+{}^2i_-{}^1$
9	11	15	18	22	25	30	31	35	36	38	36	37	32	30	23	18	10	$5)_{3/2}$	$i_+{}^4i_-{}^1$
18	22	28	33	40	44	51	55	60	61	63	61	60	53	48	38	30	17	$7)_2$	$i_+{}^5i_-{}^1$
24	31	37	46	51	60	66	73	76	81	79	80	75	70	59	51	35	24	$7)_{3/2}$	$i_+{}^6i_-{}^1$
6	6	10	10	15	15	21	21	26	24	28	24	27	21	23	15	16	6	$6)_0$	$i_+{}^3i_-{}^3$
24	29	38	44	54	59	69	72	80	80	85	80	81	70	65	49	40	21	$10)_{1/2}$	$i_+{}^4i_-{}^3$
64	83	94	116	127	149	157	177	178	192	183	188	168	163	132	118	78	57	$12)_1$	$i_+{}^5i_-{}^3$
122	152	174	207	228	260	276	302	307	322	312	312	285	268	223	191	132	90	$23)_{3/2}$	$i_+{}^6i_-{}^3$
172	199	240	268	310	333	371	384	410	406	415	390	379	331	299	231	183	101	$44)_2$	$i_+{}^4i_-{}^5$
101	119	144	166	190	210	234	246	262	266	267	257	247	219	195	157	118	70	$28)_0$	$i_+{}^4i_-{}^3$
262	314	360	418	460	513	547	584	598	616	600	589	545	500	424	355	251	163	$49)_{1/2}$	$i_+{}^5i_-{}^3$
486	573	652	742	816	895	951	1006	1028	1045	1022	991	917	836	712	587	424	268	$84)_1$	$i_+{}^6i_-{}^3$
662	760	876	977	1084	1168	1256	1302	1348	1347	1333	1269	1197	1063	929	743	556	331	$122)_{3/2}$	$i_+{}^6i_-{}^3$
692	790	916	1014	1133	1213	1312	1352	1408	1398	1394	1316	1250	1102	973	767	585	339	$133)_0$	$i_+{}^6i_-{}^4$
1262	1436	1636	1806	1992	2127	2269	2342	2410	2392	2363	2238	2102	1865	1625	1294	973	575	$210)_{1/2}$	$i_+{}^6i_-{}^4$
1679	1933	2157	2410	2604	2816	2950	3081	3113	3137	3036	2926	2688	2437	2065	1700	1219	773	$240)_1$	$i_+{}^6i_-{}^5$
2293	2595	2920	3206	3497	3723	3934	4050	4133	4099	4019	3807	3548	3158	2730	2184	1625	975	$345)_0$	$i_+{}^6i_-{}^5$
3055	3475	3857	4258	4588	4911	5129	5315	5361	5357	5189	4962	4564	4111	3495	2849	2065	1288	$412)_{1/2}$	$i_+{}^6i_-{}^5$
4108	4604	5140	5604	6069	6421	6750	6910	7022	6936	6773	6397	5950	5276	4556	3640	2704	1620	$576)_0$	$i_+{}^6i_-{}^6$

The following gives the number of combinations (C) of electron groupings, which could not be included in Table VIII:

169 $i_+{}^1i_-{}^1$	1014 $i_+{}^2i_-{}^1$	3718 $i_+{}^3i_-{}^1$	9295 $i_+{}^4i_-{}^1$
16,731 $i_+{}^5i_-{}^1$	22,308 $i_+{}^6i_-{}^1$	6084 $i_+{}^3i_-{}^3$	22,308 $i_+{}^4i_-{}^2$
55,770 $i_+{}^4i_-{}^3$	100,386 $i_+{}^5i_-{}^3$	133,848 $i_+{}^6i_-{}^3$	81,796 $i_+{}^4i_-{}^3$
204,490 $i_+{}^5i_-{}^3$	368,082 $i_+{}^6i_-{}^3$	490,776 $i_+{}^6i_-{}^3$	
511,225 $i_+{}^4i_-{}^4$	920,205 $i_+{}^5i_-{}^4$	1,226,940 $i_+{}^6i_-{}^4$	
	1,656,369 $i_+{}^5i_-{}^5$	2,208,492 $i_+{}^6i_-{}^5$	2,944,656 $i_+{}^6i_-{}^6$

TABLE IX.

Complete Terms from Equivalent i-Electrons.

C.	G.	M.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
26	i^1	2							1												
325	i^2	1	1	.	1	.	1	.	1	.	1	.	1	.	1						
		3	.	1	.	1	.	1	.	1	.	1	.	1							
2600	i^2	2	.	1	2	2	3	4	4	4	4	3	3	3	2	2	2	1	1	1	
		4	.	1	.	2	1	2	2	2	1	2	1	1	1	1	1	.			
14,950	i^2	1	4	.	8	3	10	6	11	7	12	7	11	7	9	5	7	3	5	2	3
		3	.	6	5	10	9	13	11	14	12	14	11	12	9	9	6	6	4	4	2
		5	2	.	3	2	4	2	5	3	4	3	4	2	3	1	2	1	1	.	1
65,780	i^2	2	5	11	22	26	35	38	44	44	47	44	45	41	39	34	32	26	23	18	15
		4	3	9	14	20	24	27	30	31	31	31	29	27	25	22	19	16	13	10	8
		6	2	1	4	3	6	5	7	5	7	5	6	4	5	3	3	2	2	1	1
230,230	i^2	1	16	13	40	39	63	56	79	69	84	74	81	69	77	61	63	50	50	36	37
		3	3	40	48	80	84	110	108	127	120	131	118	122	106	105	87	83	66	61	46
		5	7	13	28	31	43	45	53	52	57	52	54	48	46	39	37	29	26	20	17
		7	.	4	2	7	5	8	7	9	6	9	6	7	5	5	3	4	2	2	1
657,800	i^2	2	26	73	119	154	201	232	260	277	288	294	291	282	271	253	232	211	186	162	140
		4	16	66	97	140	164	198	210	232	233	241	231	229	210	200	177	161	137	121	98
		6	7	20	33	44	54	62	68	71	73	72	70	66	61	55	48	42	35	29	23
		8	.	4	2	7	5	8	7	9	6	9	6	7	5	5	3	4	2	2	1
1,562,275	i^2	1	49	71	161	180	261	266	333	325	372	353	380	346	361	318	317	272	264	217	206
		3	40	167	241	356	413	505	538	601	607	639	618	622	580	562	506	474	412	374	314
		5	37	77	148	180	240	261	304	310	336	325	334	311	305	273	259	222	203	168	148
		7	5	23	31	48	53	65	68	75	72	76	70	69	61	57	48	44	35	30	23
		9	2	1	4	3	6	5	7	5	7	5	6	4	5	3	3	2	2	1	1
3,124,550	i^2	2	88	244	417	551	696	802	905	969	1030	1045	1062	1040	1013	959	908	829	760	676	600
		4	78	230	373	512	630	732	818	879	918	941	938	918	885	835	774	709	636	561	490
		6	37	84	153	193	251	278	319	329	352	345	350	329	320	289	270	235	212	177	154
		8	5	17	27	36	44	51	55	58	59	58	56	53	48	43	38	32	27	22	17
		10	2	.	3	2	4	2	5	3	4	3	4	2	3	1	2	1	1	.	1
5,311,735	i^2	1	105	202	406	481	665	721	860	881	983	962	1020	969	984	907	893	796	763	662	614
		3	118	442	663	957	1136	1374	1491	1657	1703	1790	1765	1779	1694	1648	1520	1433	1281	1173	1017
		5	99	241	424	552	706	795	912	957	1021	1025	1041	1000	980	908	856	770	702	608	540
		7	18	80	114	168	193	236	248	276	274	286	272	271	246	235	206	189	159	141	113
		9	5	9	18	21	29	30	35	34	37	34	34	30	29	24	22	17	15	11	9
		11	.	1	.	2	1	2	2	2	1	2	1	1	1	1	.	1			
7,726,160	i^2	2	172	515	846	1149	1430	1674	1876	2036	2153	2220	2248	2234	2179	2095	1984	1848	1700	1542	1376
		4	156	505	795	1113	1353	1601	1771	1935	2014	2092	2085	2075	1999	1921	1788	1668	1505	1360	1193
		6	72	211	346	469	580	673	749	803	839	853	850	829	794	746	689	626	558	490	422
		8	10	51	70	106	119	148	152	171	167	175	163	163	145	139	119	109	89	79	61
		10	2	5	8	11	13	14	16	16	16	16	15	13	12	10	8	7	5	4	3
		12	.	1	.	1	.	1	.	1	.	1	.	1							
9,657,700	i^2	1	164	332	639	791	1061	1165	1386	1435	1584	1579	1661	1595	1621	1510	1481	1346	1283	1129	1053
		3	202	713	1092	1555	1870	2246	2482	2724	2826	2965	2951	2973	2860	2784	2596	2452	2221	2039	1793
		5	161	412	722	939	1201	1365	1557	1649	1763	1776	1812	1758	1722	1614	1532	1388	1276	1122	1000
		7	39	142	211	306	359	430	464	509	515	536	518	512	478	454	406	374	322	285	238
		9	10	19	38	45	61	64	75	74	80	75	76	68	66	56	52	42	37	28	24
		11	.	2	2	4	4	6	5	6	5	5	4	4	3	3	2	2	1	1	
		13							1												
10,400,600	i^2	2	231	645	1079	1456	1826	2118	2402	2590	2754	2837	2889	2860	2816	2698	2572	2398	2220	2009	1815
		4	212	636	1040	1417	1757	2056	2298	2491	2625	2701	2725	2698	2622	2510	2364	2192	2004	1805	1601
		6	105	289	467	610	778	883	1003	1059	1127	1132	1146	1106	1078	1003	943	848	772	671	591
		8	22	64	102	142	172	198	220	233	239	242	236	225	213	195	175	156	134	113	95
		10	5	5	15	14	22	20	26	23	27	23	25	20	20	15	15	10	10	6	6
		12	.	1	1	1	1	1	1	1	1	1	1	1	1						
		14	1																		

$i^{14} = i^{13}, i^{15} = i^{11}, i^{16} = i^{10}, i^{17} = i^9, i^{18} = i^8, i^{19} = i^7, i^{20} = i^6, i^{21} = i^5, i^{22} = i^4, i^{23} = i^3, i^{24} = i^2, i^{25} = i^1, i^{26} = i^0$.

1	i^{26}	1	1																		

TABLE IX.—*Continued.*

Complete Terms from Equivalent i-Electrons.

19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	*M.*	*G.*	*C.*
																								2	i^1	26
																								1 3	i^3	325
																								2 4	i^2	2600
1 2	2 1	. 1		1																				1 3 5	i^4	14,950
11 6 .	9 4 1	6 3	5 2	3 1	2 1	1	1																	2 4 6	i^5	65,780
25 41 12 1	24 29 10 .	16 25 6 1	15 16 5	8 14 3	9 8 2	4 7 1	4 3 1	2 3	.2 1	. 1	1													1 3 5 7	i^6	230,230
117 84 18 1	96 65 14 .	79 53 10 1	62 39 7	48 31 5	37 21 3	27 16 2	19 10 1	14 7 1	9 4	6 3	4 1	2 1	1	1										2 4 6 8	i^7	657,800
163 276 117 19 .	150 223 100 13 1	115 190 75 11	103 147 62 7	74 122 44 5	67 90 35 3	45 72 23 2	39 50 18 1	25 39 10 1	22 25 8	12 19 4	11 11 3	5 8 1	5 4 1	2 3	2 1	. 1	1							1 3 5 7 9	i^8	1,502,275
517 418 123 13	447 351 104 10	371 291 79 7	312 236 64 5	252 187 46 3	203 148 36 2	158 112 24 1	125 84 18 1	92 62 11	70 44 8	50 30 4	36 21 3	24 13 1	17 8 1	10 5	7 3	4 1	2 1	1	1					2 4 6 8 10	i^9	3,124,550
517 905 451 97 6	471 760 386 74 5	381 658 313 61 3	339 534 259 44 2	266 450 200 35 1	230 352 162 23 1	174 288 119 18	148 216 92 11	105 172 65 8	89 123 48 4	60 95 31 3	49 64 23 1	31 48 13 1	26 30 9	14 22 5	12 12 3	6 9 1	5 4 1	2 3	2 1	. 1	1			1 3 5 7 9 11	i^{10}	5,311,735
1214 1047 358 52 2	1056 888 298 38 1	904 759 244 31 1	764 623 195 21	637 515 154 17	521 410 118 10	422 328 89 8	336 250 65 4	262 195 47 3	201 142 32 1	153 106 22 1	112 74 14	82 53 9	58 34 5	40 24 3	27 14 1	18 9 1	11 5	7 3	4 1	2 1	1	1	2 4 6 8 10 12	i^{11}	7,726,160
900 1602 851 203 17	816 1369 737 161 14	680 1191 605 134 9	602 986 509 101 7	483 835 404 80 4	421 670 328 58 3	326 552 250 44 1	276 427 198 29 1	207 342 143 22	172 254 109 13	121 198 75 9	101 140 55 5	67 106 35 3	54 71 25 1	34 52 14 1	27 32 10	15 23 5	13 13 3	6 9 1	5 4 1	2 3	2 1	. 1	1	1 3 5 7 9 11 13	i^{12}	9,657,700
1597 1401 496 76 3	1401 1209 424 60 3	1203 1025 343 47 1	1027 859 283 35 1	854 707 220 25	712 573 176 19	574 457 130 12	464 359 100 8	364 275 70 6	284 209 52 3	214 154 34 1	164 112 24 1	118 79 14	86 55 10	60 36 5	42 24 3	27 15 1	19 9 1	11 5	7 3	4 1	2 1	1	1	2 4 6 8 10 12 14	i^{13}	10,400,600

$i^{14} = i^{12}$, $i^{15} = i^{11}$, $i^{16} = i^{10}$, $i^{17} = i^9$, $i^{18} = i^8$, $i^{19} = i^7$, $i^{20} = i^6$, $i^{21} = i^5$ $i^{22} = i^4$, $i^{23} = i^3$, $i^{24} = i^2$, $i^{25} = i^1$

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

RESEARCH PROGRAM ON BUILDING MATERIALS AND STRUCTURES.

Congress recently granted to the Bureau $198,000 for the fiscal year 1937–38 to study the properties and suitability of building materials with particular reference to their use in low-cost housing. A general statement has just been released outlining the objectives, procedure, and scope of the program. Copies of this statement, Letter Circular LC502, Research Program on Building Materials and Structures, 1937–38, may be obtained from the Bureau on request.

The program is being formulated with the advice of representatives of the housing agencies of the Government. The sub-committee on design and construction of the Central Housing Committee has designated a special group to co-operate with the Bureau on this program of technical research. The group consists of Harold D. Hynds, chairman, C. W. Chamberlain of the Procurement Division, Pierce Blouke of the Home Owners' Loan Corporation, Walter Junge of the Federal Housing Administration, Charles Mayette of the Public Works Administration, Vincent B. Phelan of the National Bureau of Standards, Colin O. Skinner of the Resettlement Administration, George W. Trayer of the Forest Service, Capt. Elsmere J. Walters of the Quartermaster Corps of the Army.

The conduct of the program is entrusted to a committee of Bureau division chiefs, P. H. Bates, H. C. Dickinson, H. L. Dryden, W. E. Emley, G. E. F. Lundell, A. S. McAllister, and H. S. Rawdon, under the chairmanship of H. L. Dryden, who is designated as coordinator of the program.

The general objective of the work is to furnish to government agencies, the building industry, and the public, technical information from every available source on the engineering properties of building materials as incorporated in the struc-

* Communicated by the Director.

tural elements and equipment of a house, with particular reference to low-cost housing. This includes new materials, equipment, and methods of construction as well as those already in use. The program will not deal with sociological, economic, hygienic, or esthetic questions, or with architectural design. The Bureau does not expect to prepare new house plans.

The detailed programs of the studies on bearing walls, partitions, floors, roofs, heating and ventilating equipment, and plumbing, suitable for use in low-cost housing are now being prepared. Conferences have been held between designated representatives of other government agencies and selected groups of Bureau personnel on the structural properties of low-cost construction; thermal insulation, moisture condensation, and heating and ventilating problems; plumbing; corrosion of steel; weather-tightness of roofs; finish floors; building papers and boards; wiring and lighting.

TOOTH PASTE SPECIFICATION.

There has recently been adopted by the Government a specification for tooth paste in which thorough laboratory work and service tests are represented, a committee of the Federal Specification Executive Committee having charge of the preparation of this specification.

From the point of view of health and money value, a specification for this commodity is of the utmost importance. The Government itself is a large purchaser of this material, a recent order calling for over 150,000 tubes having been placed by one department.

The specification is not a complex one, but it does set forth definite requirements as to what may or may not go into the Government's tooth paste, and it states how tests shall be conducted. The specification covers: Types; materials and workmanship; general and detailed requirements; methods of inspection and test; packaging, packing, and marking; and special requirements applicable to various Government departments.

During the course of the investigation, it was found that of 25 popular brands of tooth paste, all of which contained

special materials for which some benefit was claimed, 10 failed to pass the abrasion test now incorporated in the specification, and 11 failed for other reasons. Tests of this kind assist manufacturers by identifying the undesirable ingredients, resulting in their elimination and consequent improvement of the product.

The abrasion test, which is but one of the tests included in the specification, is a very important one because any material which will abrade human enamel must be kept out of a tooth paste. By merely grinding a paste between the teeth, it is possible for an experienced observer to detect one per cent. of emery in a paste, but the test in the new Government specification, which was developed at the Bureau, will detect the presence of emery or materials having similar abrasive qualities if present in amounts of one part in 100,000, or one thousandth of one per cent. Even so, the test for abrasives is simple, as will be noted from the following:

> "E-5. The tooth paste shall not scratch glass." "F-1e (1). Tooth paste shall be placed on glass and rubbed with a copper alloy similar in composition and shape to the 5 cent coin which has previously been rubbed against glass without scratching. The glass shall be of the usual soda-lime grade such as is used in non-corrosive microscope slides."

Limits are set for acidity and alkalinity values.

The Government has found that the use of Federal Specification FFF–D–191 will enable its purchasing officers to secure a satisfactory article on the basis of free competition and at the lowest price consistent with the necessary quality. Copies are obtainable at 5 cents each from the Superintendent of Documents, Government Printing Office, Washington, D. C.

Any manufacturer who is certain that his product complies with Federal Specification FFF–D–191 is at liberty to say so on the label of his product. Such marking would give to the general public many of the benefits which will be secured by the Government.

The Bureau does not make routine or commercial tests of tooth paste, except for other branches of the Government.

Any well equipped chemical testing laboratory can make the necessary tests for compliance with the specification.

A report of the investigation was presented at a recent meeting of the American Dental Association and will be published in an early number of their *Journal*. Trade names are not mentioned in the report.

MEASUREMENT OF FLAME SPEEDS IN ENGINE CYLINDERS.

Although the modern internal-combustion engine has attained a high state of mechanical development, many important details of its combustion process remain obscure. There is need for a better understanding of the micromechanism of flame propagation, and of the effects of operating factors on the speed at which flame propagates through the explosive charge. In recognition of this, the National Advisory Committee for Aeronautics has sponsored research at the Bureau to obtain fundamental information on gaseous explosions. A paper by Ernest F. Fiock and Charles F. Marvin, Jr., which was presented at the American Chemical Society's meeting in September reviews past work and outlines the present program at the Bureau.

Flame speeds have been measured during explosions at constant pressure and at constant volume. In the constant-pressure method, which has been in use for a number of years, a soap bubble is blown with explosive mixture and fired by a spark at its center. The spark initiates a tiny sphere of flame which grows rapidly, maintaining its spherical shape, until all of the mixture is burned. The travel of the flame is recorded on a moving film and the photograph is analyzed to show the speed of the flame front in space and with respect to the unburned charge. This method, which is relatively simple and accurate, has been used successfully to study the effects of changes in fuel-oxygen ratio and dilution of the charge with inert gases, but is adapted only to a limited range of conditions.

The constant-volume method, in which explosions occur in a closed bomb, although more complicated, permits investigation of the independent effects of pressure, temperature, and charge composition over a much wider range of condi-

tions. In this method the movement of the flame and the accompanying rise in pressure must both be recorded if the rate of flame propagation with respect to the unburned gas is to be determined. A spherical steel bomb with central ignition and auxiliary equipment for obtaining simultaneous records of flame travel and pressure rise has been constructed and experiments are now in progress. It is hoped that the data obtained will clarify the mechanism of flame propagation and suggest practical means for further control of gaseous explosions.

HEATS OF COMBUSTION OF ETHYLENE AND PROPYLENE.

Ethylene and propylene are two hydrocarbon gases which have become very important within recent years, because of their availability (of the order of 100,000,000,000 cubic feet annually) as by-products from the "cracking" processes of the petroleum industry, because of their use in the synthetic production of alcohols and other chemical substances, and because of their utility in the making of motor fuel of high anti-knock value by the newly developed polymerization processes.

If such processes are to be carried on most economically and profitably, there must be known accurate values for the heats and free energies of formation of these substances. Notwithstanding the importance of ethylene and propylene in these industrial processes, their existing values of heats of formation depend upon measurements made about half a century ago. Because data obtained at the Bureau several years ago showed that the old "accepted" value for the heat of combustion of ethane was in error by about 4 kilo calories per mole, it was suspected that the old "accepted" values for ethylene and propylene might also be seriously in error. A redetermination of these two important thermodynamic constants was therefore undertaken by Frederick D. Rossini and John W. Knowlton, and the work which has now been completed, is reported in the *Journal of Research* for September (RP1024).

The results of these new measurements show, for ethylene, a discrepancy even more startling than that previously found

for ethane. The new value for ethylene differs by about 5 kilo calories per mole from the old "accepted" value, and the new value for propylene differs by about 2 kilo calories per mole from its old "accepted" value. In terms of the heat evolved in the combustion of the gas in oxygen to form gaseous carbon dioxide and liquid water, all at 25° C. and a constant pressure of 1 atmosphere, the new values are: ethylene, 337.28 ± 0.07 kilocalories per gram-mole; propylene, 491.82 ± 0.15 kilocalories per gram-mole.

PHYSICOCHEMICAL CONSTANTS OF BENZENE.

RP1029 by Mieczyslaw Wojciechowski, in the September number of the *Journal of Research*, describes recent measurements of certain physicochemical constants of benzene.

Benzene was purified by four different methods resulting in a number of preparations of a very high degree of purity. The following physicochemical constants were measured: Boiling point 80.094°, freezing point 5.51° C.; refractive index n^{25} 1.49807; and density at 25° 0.87366 g./cm³. Previous determinations of these constants, as reported in the literature, are also reviewed in this paper. The work shows that benzene can be obtained in a state of purity sufficiently high to warrant its use as a secondary standard substance for determining physicochemical constants by comparative methods.

EXTRACTION OF LEVULOSE FROM JERUSALEM ARTICHOKES.

Experiments conducted at the Bureau in 1925 by Proffitt, Bogan, and Jackson first demonstrated that the natural levulose compounds, or polysaccharides, contained in the tubers of jerusalem artichokes, can be extracted through the medium of hot water in the apparatus known as the diffusion battery. In this process, as in the diffusion of cane sugar from beets in the same type of equipment, a considerable proportion of the extractives is transferred from the plant substance into the water by dialysis through the vegetable tissues. Since the polysaccharides are composed mainly of molecules which are exceedingly large compared with the molecules of cane sugar, it is interesting to find that the rate of extraction never-

theless is comparable with the rates obtained in the diffusion of cane sugar from beet cossettes, and that the resulting residues of the extractives in the pulp and pulp water discarded from the process can be reduced to a feasible degree, involving no excessive rejectment of levulose. Experiments recently conducted by Max J. Proffitt, John A. Bogan, and Richard F. Jackson, indicate that the pulp can be pressed and dried, yielding a quantity of dried pulp equal to about 4.3 per cent. of the weight of the original artichoke cossettes. This is somewhat less than the average yield of dried beet pulp from beet cossettes, but analysis indicates that the dried artichoke pulp should have a feeding value for live-stock which is superior to that of beet pulp.

A more complete account of this work will be published as RP1025 in the September number of the *Journal of Research*.

CORROSION OF METALS IN SOILS.

In the design of any underground metallic structure, such as a pipe line, one of the important considerations is the rate at which the metal is corroded by the soil. Usually the builder may choose between several ferrous materials, and in some cases it is even possible and economical to use nonferrous metals such as copper and lead. Bituminous, metallic and other types of coatings may also be used to protect the pipe line.

The relative merits of the commonly used ferrous materials, cast iron, wrought iron, and steel has been a controversial question for many years. There is no essential reason why any one of the wrought ferrous materials should be superior to the others, because the composition and structure of all of them are essentially similar. However, it is of considerable importance to know whether the corrosion resistance of these alloys can be improved by adjusting their composition within the limits of good manufacturing practice.

Dr. Scott Ewing, research associate of the American Gas Association, has compared the composition of the 8 wrought ferrous materials in the soil corrosion test of the National Bureau of Standards with the average pitting rate over a period of exposure of 12 years in 23 test sites. The only

alloying element which appears to have any effect on the pitting rate is phosphorus. The pitting rate decreases slightly as the phosphorus content is increased up to about 0.1 per cent. This result is in rough accord with the atmospheric corrosion test results of the American Society for Testing Materials.

The conditions in soils which cause corrosion of lead and copper have also been considered, using the Bureau's results for these metals. Lead, while usually more resistant than the ferrous metals, is pitted to greater depth in 6 out of 47 test locations. In these soils the content of sulphates is very low and the soil is about neutral (pH7) in reaction. Lead is practically unaffected in soils containing large amounts of sulphates. Copper is in general more resistant than either lead or steel. It is seriously attacked in cinders and tidal marshes. In soils containing relatively large amounts of chloride and carbonates the attack of copper is appreciable but usually not serious.

Heavy zinc (galvanized) coatings have been found to afford good protection to steel pipes under the conditions of the tests, while lead-coated steel is usually seriously pitted. The essential reason for this difference in these metals is that zinc is anodic to steel while lead is cathodic.

THE FRANKLIN INSTITUTE.

LIBRARY NOTES.

The library and reading room are open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays two until ten o'clock P.M. 484 readers made use of the facilities during the twenty-six days of August.

RECENT ADDITIONS.

Agriculture and Forestry.

GRAY, GEORGE DOUGLAS. All About the Soya Bean. 1936. Welsh Journal of Agriculture. Volume 13. 1937.

Aviation.

LEHMANN, ERNST A. Zeppelin. The Story of Lighter-than-Air Craft. In Collaboration with Leonhard Adelt. Translated by Jay Drather. 1937.

Chemistry and Chemical Technology.

HERFELD, HANS. Lederdeckfarbenzurichtung und Lacklederherstellung. 1936.

Jahresbericht über die Leistungen der chemischen Technologie für das Jahr 1936. 82 Jahrgang. 1. Abteilung: Unorganischer Teil. 1937.

KUBLUN, HELMUT. Kiefernharznutzung mit chemischen Reizmitteln. 1936.

MULDOON, HUGH C. A Textbook of Organic Chemistry for Students of the Medical Sciences. Second Edition. 1936.

Society of Chemical Industry. Chemical Engineering Group. Proceedings 1935–1936. Volumes 17–18. 1936–1937.

WEBER, HANS H. Praktische Lösungsmittelanalyse. 1936.

Directories.

Combustion Appliance Makers' Association. The Black Book. A Directory of Solid Fuel-Burning Appliances and Associated Equipment. 1937 Edition.

Electricity and Electrical Engineering.

DOW, WILLIAM G. Fundamentals of Engineering Electronics. 1937.

GURNEY, R. W. Ions in Solution. 1936.

KAPPELMAYER, OTTO. Fernsehen von Heute. Die Vorgänge beim Fernsehen. 1936.

LANGER, MAX. Studien über Aufgaben der Fernsprechtechnik. 1936.

World Power Conference. Statistical Year-Book No. 1, 1933 and 1934–1936.

Geology.

Great Britain. Imperial Institute. Mineral Resources Department. Platinum and Allied Metals. Second Edition. 1936.

Union of South Africa. Department of Mines. The Mineral Resources of the Union of South Africa. 1936.

Hygiene and Physiology.

LEWIS, SIR THOMAS. Clinical Electrocardiography. Sixth Edition. 1937.

PRAUSNITZ, C. Investigations on Respiratory Dust Diseases in Operatives in the Cotton Industry. 1936. Medical Research Council. Special Report Series No. 212.

Manufactures.

WINKLER, LUDWIG, AND RICHARD ERNST. Die Spiegelfabrikation. 1936.

Mathematics.

SNYDER, VIRGIL, AND C. H. SISAM. Analytic Geometry of Space. 1914.

VEBLEN, OSWALD, AND JOHN WESLEY YOUNG. Projective Geometry. Two volumes. 1910–1918.

Metallurgy.

Aluminium-Zentrale. Aluminium-Taschenbuch. Siebente Auflage. 1937.

Military Engineering.

Socialist Medical Association. Gas Attacks. Is There Any Protection? 1936.

Physics.

JONES, ARTHUR TABER. Sound. A Text-book. 1937.

SHRADER, J. E. Manual of Experiments in Physics. First Edition. 1937.

SHRADER, J. E. Physics for Students of Applied Science. First Edition. 1937.

Sociology.

FELDMAN, HERMAN. Problems in Labor Relations. 1937.

Sugar.

KNÖCHEL, E. Fachwörterbuch für die Zuckerindustrie. Deutsch-Italienisch und Italienisch-Deutsch. 1936.

Welding.

British Standards Institution. British Standard Specification for Oxy-Acetylene Welding as Applied to Steel Structures. 1936.

Welding and Cutting Year-Book. 1936–37.

BOOK REVIEWS.

THEORY OF ALTERNATING-CURRENT MACHINERY, by Alexander S. Langsdorf. First edition, 788 pages, illustrations, 16 × 23.5 cms. New York, McGraw-Hill Book Company, Inc., 1937. Price $6.00.

The importance of a good text on the fundamentals of any of the subjects in electrical engineering cannot be overestimated. Electric power engineers in practice over a period of many years often recall the distinct impressions that many passages of such a text have made and these impressions lead to solutions of problems that otherwise would be difficult if at all possible to solve. Not only because of this but because of the ready reference afforded do these engineers hold the text in high value. It is paramount therefore that the student be watchful of the textbooks selected for his training.

The book at hand belongs to this class of basic texts. It deals with and is limited to electromagnetic machinery. The author makes special effort to dispel the spectre of mystery that sometimes arises in the minds of students reaching the point in their studies preparatory to taking up alternating current machinery. To do this he has begun his book in the realm of the generation of electromotive force by the rotation of a coil in a magnetic field and gradually proceeds to show very clearly current and voltage relations. Then in a brief respite there is given a treatment on vector notation and its application to the solution of alternating currents. This is held up as a working tool for use in the rest of the book. Returning again to elements of generation, polyphase circuits are taken up.

The treatment so far may be viewed as making way for the study of electromagnetic machinery proper. This study, like some of the older well known texts, uses the transformer as the starting point for all of the other types of machines covered. Following the transformer, synchronous machines are explained, their theory and operation—generators, motors and the synchronous converter. The part of the book on asynchronous machines begins with a consideration of principles, based upon physical considerations, which are common to many or all of them. A mastering of these principles as here given makes it possible to study any kind of machine of this type in any order whatever. Single and polyphase induction motors, the induction generator, and commutator motors completes the text.

The approach to each topic and its subsequent handling reveal a keen insight into the situation and needs of the student. Carefully composed problems for each chapter are given at the end of the book. A subject index adds much value for reference purposes.

R. H. OPPERMANN.

HANDBOOK OF CHEMISTRY, compiled and edited by Norbert Adolph Lange, assisted by Gordon M. Forker. Second edition, 1778 pages, 14 × 20.5 cms. Sandusky, Ohio, Handbook Publishers Inc., 1937. Price $6.00.

The first impression we receive upon opening this handbook is that the presentation of the material is handled in unusually fine style. The type is excellent and the data given are not crowded on the page. The book is well bound and the paper is of satisfactory quality.

This second edition of the handbook gives a number of new tables which were not included in the first edition. Among these are tables of organic ring systems, formula index to the compounds listed in the table of physical constants of organic compounds, melting points of organic compounds arranged in ascending order of melting points, various tables of refractive indices, viscosity of aqueous glycerol solutions for calibration of viscosimeters, and denatured alcohol tables.

If the book has a fault, it is perhaps that it attempts to cover too much ground. In the opinion of the reviewer, some of the tables could have well been omitted in a book of this sort. To replace these omitted data, the reviewer would suggest amplifying some of the tables of physical constants by means of recent data taken from the journal literature.

This handbook is well worth the price asked, six dollars, and can be heartily recommended to the student, scientist, or dabbler in science who requires an extensive and well edited book of its type.

GEORGE S. GARDNER.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 596, Cooling Tests of a Single-Row Radial Engine with Several N. A. C. A. Cowlings, by M. J. Brevoort, George W. Stickle, and Herman H. Ellerbrock, Jr. 10 pages, illustrations, tables, 23 × 29 cms. Washington, Government Printing Office, 1937. Price ten cents.

The cooling of a single-row radial air-cooled engine using several cowling arrangements has been studied in the N. A. C. A. 20-foot wind tunnel. The results show the effect of the propeller and several cowling arrangements on cooling for various values of the indicated horsepower in the climb condition. A table giving comparative performance of the various cowling arrangements is presented. The dependence of temperature on indicated horsepower and pressure drop across the baffles is shown by charts. Other charts show the limiting indicated horsepower against the pressure drop across the engine and the heat dissipated at various values of the indicated horsepower.

Report No. 598, Alternating-Current Equipment for the Measurement of Fluctuations of Air Speed in Turbulent Flow, by W. C. Mock, Jr. 18 pages, illustrations, 23 × 39 cms. Washington, Government Printing Office, 1937. Price ten cents.

Recent electrical and mechanical improvements have been made in the equipment developed at the National Bureau of Standards for the measurement of fluctuations of air speed in turbulent flow. Data useful in the design of similar equipment are presented. The design of rectified alternating-current power supplies for such apparatus is treated briefly, and the effect of the power supplies on the performance of the equipment is discussed.

QUANTITATIVE ORGANIC MICROANALYSIS OF FRITZ PREGL, by Dr. Hubert Roth. Third English Edition, 270 pages, illustrations, plates, tables, 15.5 × 25.5 cms., Philadelphia, P. Blakiston's Son & Co. Inc., 1937. Price $5.00.

This third English edition, translated from the fourth German edition of Pregl's Quantitative Organic Microanalysis represents a complete and intelligent revision of Pregl's classic work. The new edition is a necessity because of the rapid strides taken in the past few years by the new science of microanalysis.

Numerous improvements in arrangement and discussion of methods are evident throughout the volume. The illustrations have been increased from 51 to 72 and the size has been increased from 232 pages to 267 pages. The revision, however, has not been merely an addition of some new material. The book has been brought up to date, even to the smallest detail.

New methods of determination described in the recent edition are: "The alkalimetric determination of chlorine and bromine; the titration of iodine as iodata; the volumetric determination of sulphur in the presence of nitrogen and halogen; the determination of barium and phosphorus and of nitrogen and mercury, respectively, in the presence of each other; the direct determination of equivalent weights; the determination of "active hydrogen," the titration of amino acids; the volumetric determination of alkoxyl and alkyl amino groups, and of methyl groups attached to sulphur; a simplified determination of acetyl and benzoyl groups and the determination of methyl groups attached to carbon, as acetic acid; the determination of isopropylidene groups attached to oxygen and

carbon, as acetone; catalytic microhydrogenation; photoelectric measurement of the absorption spectra; micro-molecular refraction; determination of molecular weight by isothermal distillation; determination of melting points under the microscope and of boiling points with very small amounts of material."

GEORGE S. GARDNER.

CARL FRIEDRICH GAUSS. Inaugural Lecture on Astronomy and Papers on the Foundations of Mathematics, translated and edited by G. Waldo Dunnington. 91 pages, illustrations, 14 × 20 cms. Baton Rouge, Louisiana State University Press, 1937. Price $1.00.

The story of genius is fascinating, particularly when the work refers to a familiar field. The contributions made to mathematics and astronomy by Carl Friedrich Gauss can never be overlooked. This little monograph is not a complete story of the life of Gauss but it does give a rather thorough sketch of what is known of his early life. The sketch, composed of biographical notes is followed by an introductory note to Gauss' meditations on the foundations of mathematics which explains and prepares for the subsequent paper itself. The book contains another introduction and a lecture on astronomy. The papers are interesting and important and should enrich the knowledge of the work of this great man.

R. H. OPPERMANN.

TEXTBOOK OF THERMODYNAMICS, by Paul S. Epstein. 406 pages, illustrations, tables, 16 × 23.5 cms. New York, John Wiley & Sons, Inc., 1937. Price $5.00.

A new textbook on thermodynamics is interesting to go through because the subject has a certain fascination for many who are familiar with it. It refreshes the memory and knowledge, and perhaps makes deeper impressions. But to examine a number of texts on the same subject in somewhat rapid succession without having a definite object in view becomes boresome unless entirely different approaches to the contents are encountered. This is exactly what the author of this book has attempted to do—to treat the subject from the point of view of the physicist. He states in the Preface, "There appeared in recent years some excellent textbooks dealing with the chemical applications of thermodynamics but, in relation to physics, this field has been neglected for nearly thirty years. The reason for this neglect, undoubtedly, was the rise to prominence of the statistical theory of matter which induced many teachers to offer in a single course a combination of thermodynamics and statistical mechanics. However, as these two disciplines developed, they extended their range of applications and enlarged their subject matter to the point where the joint treatment became more and more cumbersome."

The book is divided into twenty-two chapters so constructed that it is flexible enough for use in teaching under various programs. The first part is a basic text and the rest more advanced. The first and second laws are treated, which is followed by discussions on equilibrium, phases of chemically pure substances, gaseous mixtures, dilute solutions, and fugacities and activities. Nernst's heat postulate or the third law of thermodynamics is then taken up including its bearing on the absolute entropy of gases, and a critical analysis of Nernst's postulate. Degenerate perfect gases, electron and ion clouds, specific heat theory, magnetic

and electric phenomena, the direction of thermodynamical processes, and limitations of thermodynamics are topics which complete the text. Appendix I contains a comparative table of thermodynamical notations and there is a subject index.

The main feature of the book is the new angle of approach. Because of this it warrants close examination by teachers as well as by those whose daily activities are in line with the subject matter.

R. H. OPPERMANN.

ELECTRICAL OCCUPATIONS, by Lee M. Klinefelter. 227 pages, illustrations, 13.5 × 20 cms. New York, E. P. Dutton and Company, Inc., 1937. Price $2.00.

It is not very often the case that boys in high school look forward to what is in store for them after graduation. The young mind, if left to itself, generally lacks the ability to definitely plan future activities over long periods, i.e. to prepare for the "long pull" with respect to lifetime occupations. This is probably due to having had no experience and the absence of a guide or other means of assistance. It is true that some boys are fortunate enough to be in a position to follow in their father's business or to have a college education that may be in line with their tendencies. All boys, however, need a guiding hand in the way of encouragement and method in the selection of a lifetime occupation.

This book surveys the possibilities for boys in the electrical industry. Based on the thought that happiness in work is found in the natural inclination toward it, the author gives in the form of a narrative a worth while plan of attack on the problem. The story is written around an average boy in high school whose father is doubtful as to the possibility of a college training. In the beginning it is assumed that the boy has a liking for electrical work. There is no question raised regarding the reason for this liking—whether it be only because of observance of spectacular electrical operations and developments or whether the interest be genuine enough to carry through the difficult periods of a lifetime occupation. In this respect, the plan presented may be classed as a test, for it will bring out the answer.

After carefully weighing all of the advantages of positions in general, the boy and his father set out to investigate different positions in the electrical industry both for the high school graduate and the college trained engineer. They hear the stories of those who are employed as engineers and workers in the electric power supply business, the telephone, the radio, and the electric storage battery business, electrical drafting, motion picture projection, welding, and opportunities in the U. S. Army and Navy. Very pertinent information is found out about each field. This includes the nature of the work, how much it pays, opportunities for advancement, regularity, age limits, education required and how it may be obtained, and other advantages such as hours of work, pensions, social position etc.

The book is as much for parents as it is for boys. It is valuable not only for boys inclined to electrical studies but for others as well, as it offers a method for the solution of a very important problem that confronts all.

R. H. OPPERMANN.

THE ADVANCING FRONT OF SCIENCE, by George W. Gray. 364 pages, illustrations, 16 × 24 cms. New York, McGraw-Hill Book Company, Inc., 1937. Price $3.00.

Even today there are some who, like the Harvard professor of 1895, believe that all fundamental conceptions of scientific truth are found and only details remain to be filled in. There are others today who feel that there is a wide gap between what is sometimes called pure research, and actual production for human use and consumption. We do not need to look far to find those who have these impressions and curiously enough they are still found among the "intellectuals" as well as the "common people." There is, however, a class who have made and are making an earnest effort to dispel these ideas and, through education, establish the truth of what is taking place by interpretation and translation of the "technical stuff" so that all may understand and appreciate. Museums containing apparatus in operation and having accompaning lectures for the public, are evidences of this. So too, among this class, are authors of books designed for this purpose.

The book at hand will provide interesting reading to the average individual. At the same time it is informative. The author's fundamental task is to impress very strongly that the geographic pioneer and explorer so common of yesterday is now replaced to a great extent by the modern explorer who copes with new frontiers, the frontiers of the truth about nature. Innumerable vivid illustrations are given to show the romance and the lure of this new and fruitful activity of man.

The story is an account of the more up-to-date status of science and scientific investigation. In order to do this the author provides brief sketches of a historical nature so that there is made distinct the border region between the known and the unknown in an understandable way. The reader will have no difficulty in grasping the story of the gradual receeding horizons or frontiers as man's knowledge of nature has progressed to the present time. Nor will he have any doubt that such pursuit in the realm where there is no immediate commercial return in sight, brings much in the way of better living for all of us. The book covers astronomy, physics, chemistry, electricity, and combinations of various parts of these subjects which have more recently been the cause of some astounding discoveries.

Written in a manner that is easily readable, this book is one of a class that should be read at the earliest opportunity. It is outstanding in that present frontiers are stressed primarily or, in other words, it surveys and informs on the state of the progress of science as it is today.

R. H. OPPERMANN.

THERMODYNAMICS, by Enrico Fermi. 160 pages, illustrations, 15 × 23 cms. New York, Prentice-Hall, Inc., 1937.

This is a textbook of 155 pages that originated in a course of lectures at Columbia University during the summer of 1936. It is meant for those who are well grounded in the fundamental facts of thermometry, calorimetry and allied subjects.

In the introduction it is stated that the actual basis for the equivalence of heat and dynamical energy is to be sought in the kinetic interpretation which reduces all thermal phenomena to the disordered motions of atoms and molecules and from this point of view, the study of heat must be considered as a special

branch of mechanics. On the other hand the approach in pure thermodynamics is different. Here the fundamental laws are assumed as postulates based on experimental evidence, and conclusions are drawn from them without entering into the kinetic mechanism of the phenomena. Both procedures have their advantages.

The text begins with the study of thermodynamic systems in general, then proceeds through the first and second laws, the entropy, thermodynamical potentials, gaseous reactions, and dilute solutions. The Nernst addition of a third law is taken up lastly, in terms of statistical interpretation.

For a short and clear text on the fundamentals of the subject the book may be recommended.

R. H. OPPERMANN.

ASPECTS OF SCIENCE, by Tobias Dantzig. 285 pages, illustrations, 14 × 21 cms. New York, The Macmillan Company, 1937. Price $3.00.

Those of us who are given to viewing things in their entirety from long range have often, during leisure hours, made an effort to answer the query on the why of scientific reasonings, and where is the quest for greater scientific knowledge leading us. Our thoughts wander from the present back through the past, to great discoveries by famous men, to the early periods when much of what we know today was attributed generally to mysterious phenomena. We try to determine why man has sought for solutions for such activities and reactions. Conclusions, by following this line of thought, if at all reached are of a large variety.

This book is meant for such thinkers. The trend of thought and reasonings are similar. It is an attempt to disentangle much that is pertinent of the great mass of facts and supposed facts which are bound to clutter such musings. Scientific and religious outlooks are examined, their differences discussed, and their influence on the rate of progression of new ideas. The author discusses the birth and results to a limited extent of the age of experimentation and the part that mathematics plays in the general scheme, which leads to further discussions.

There are bound to be many violent disagreements on the theme presented here, in its entirety as well as with many details. The tale of science versus religion is not new, but the critical analysis of science primarily, of the bearing of religion secondarily, and the final weighing of one against the other as here presented, is of interest and should be given a hearing. If the book does nothing else, it will stimulate thought.

R. H. OPPERMANN.

AUTO-RADIO POCKET TROUBLE SHOOTER "GADGET," by Alfred A. Ghirardi. 24 pages, 13 × 18 cms. New York, Radio & Technical Publishing Co., 1937. Price $.50.

HOME-RADIO POCKET TROUBLE SHOOTER "GADGET," by Alfred A. Ghirardi. 18 pages, 13 × 18 cms. New York, Radio & Technical Publishing Co., 1937. Price $.50.

These cleverly constructed card indexes are a means for indicating causes of trouble experienced in radio receivers. There are two such indexes, one for the auto-radio and one for the home-radio. Each consists of a number of cards

clamped together in the lower right hand corner. Along the upper edge there are two rows of tabs on which there is printed the various trouble symptoms such as, dead receiver, intermittent reception, fading, etc. Along the right hand edge of the cover card there are blocked various possible trouble sources such as antenna system, battery, tubes, etc. The idea is to select the tab containing the correct trouble symptom, then pull that card to the right so its ruled lines line up with the lines of the blocks on the cover card. On the tab or symptom card then can be read all the possible troubles that may be causing the trouble symptom. The scheme is ingenious and, no doubt in the majority of cases, will indicate receiver troubles and their solution.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

The Structure and Composition of Foods, by Andrew L. Winton and Kate Barber Winton. Volume III, Animal Products. 524 pages, tables, illustrations, 15 × 24 cms. New York, John Wiley & Sons, Inc., 1937. Price $8.00.

The Advancing Front of Science, by George W. Gray. 364 pages, illustrations, 16 × 24 cms. New York, McGraw-Hill Book Company, Inc., 1937. Price $3.00.

Aspects of Science, by Tobias Dantzig. 285 pages, illustrations, 14 × 21 cms. New York, The Macmillan Company, 1937. Price $3.00.

Transactions of The American Institute of Mining and Metallurgical Engineers, Volume 124, Institute of Metals Division, 1937. 398 pages, tables, illustrations, 16 × 23 cms. New York, Institute, 1937. Price $5.00.

Astronomy for the Millions, by Prof. G. Van Den Bergh, translated from the Dutch by Joan C. H. Marshall and Th. de Vrijer. 370 pages, illustrations, 15 × 21 cms. New York, E. P. Dutton and Company, Inc., 1937. Price $3.50.

Electrical Occupations, by Lee M. Klinefelter. 227 pages, illustrations, 13.5 × 20 cms. New York, E. P. Dutton and Company, Inc., 1937. Price $2.00.

Thermodynamics, by Enrico Fermi. 160 pages, illustrations, 15 × 23 cms. New York, Prentice-Hall, Inc., 1937.

Foundations of College Physics, by Samuel Robinson Williams. 630 pages, plates, illustrations, tables, 15 × 23 cms. Boston, Ginn and Company, 1937. Price $4.00.

United States Department of Interior, Minerals Yearbook, 1937, compiled under supervision of H. H. Hughes, Economics and Statistics Branch. 1502 pages, tables, illustrations, 15 × 23 cms. Washington, Government Printing Office, 1937. Price $2.25.

Handbook of Chemistry, compiled and edited by Norbert Adolph Lange, assisted by Godon M. Forker. Second edition, 1778 pages, 14 × 20.5 cms. Sandusky, Ohio, Handbook Publishers Inc., 1937. Price $6.00.

Diffusion und Chemische Reaktion in Festen Stoffen, von Dr. Wilhelm Jost. 231 pages, illustrations, tables, 15 × 23 cms. Dresden, Verlag Von Theodor Steinkopff, 1937. Price, 20 R.M. (Die Chemische Reaktion, Band II.)

Canada Department of Mines and Resources, The Canadian Mineral Industry in 1936, Reviews by the Staff of the Bureau of Mines. 78 pages, illustrations, tables, 16 × 25 cms. Analyses of Coals and other Solid Fuels—1934 to 1936,

compiled by J. H. H. Nicolls and C. B. Mohr. 139 pages, 16 × 25 cms. Ottawa King's Printer.

Bell Telephone Laboratories, Scientific Research Applied to the Telephone Transmitter and Receiver, by Edwin H. Colpitts. 24 pages, illustrations, tables. Monographs: B-1000, A Simplified Circuit for Frequency Substandards, by S. C. Hight and G. W. Willard. 15 pages, illustrations. B-1001, Electrochemical Techniques in Corrosion Study, by R. M. Burns. 14 pages, illustrations. 3 pamphlets, 15 × 23 cms. New York, Bell Laboratories 1937.

National Advisory Committee for Aeronautics. Technical Notes: No. 608, Free-Spinning Wind-Tunnel Tests of a Low-Wing Monoplane with Systematic Changes in Wings and Tails, I. Basic Loading Conditions, by Oscar Seidman and A. I. Neihouse. 17 pages, illustrations. No. 608, Considerations Affecting the Additional Weight Required in Mass Balance of Ailerons, by W. S. Diehl. 12 pages, illustrations, tables. No. 610, Effect of Air-Entry Angle on Performance of a 2-Stroke-Cycle Compression-Ignition Engine, by Sherod L. Earle and Francis J. Dutee. 26 pages, illustrations. No. 611, The Sonic Altimeter for Aircraft, by C. S. Draper. 121 pages, illustrations, plates. 4 pamphlets, 20 × 26 cms. Washington, Committee, 1937.

CURRENT TOPICS.

Semi-Outdoor Station Placed in Service.—(*Combustion*, Vol. 8, No. 2.) A new steam-electric generating station embodying unusual features of design was placed in operation recently by the Utah Power and Light Company. Located on the Provo River near Olmsted, Utah, about 50 miles from Salt Lake City at an elevation of nearly 5,000 feet, this plant of semi-outdoor construction will supplement the hydro power of the company's system. It is laid out on the single unit plan and consists of one boiler supplying steam at 400 lb. pressure, 750° F. temperature to an 18,750 kw. General Electric condensing turbine generator with 3 point bleed for feedwater heating. An outdoor coal storage field of 7,500 tons capacity is located adjacent to the plant. By enclosing only that portion of the steam-generating unit that must be constantly accessable for operation and by making the turbine room only 17 feet from floor to bottom of roof steel, an appreciable saving was effected in building cost, despite the additional expense incurred in protecting the exposed parts from the elements.

R. H. O.

Gas Fired Diesel.—(*Power*, Vol. 81, No. 9.) In areas where gas fuel is plentiful and cheap a readily convertable engine is in demand. Many attempts have been made to burn gas in a 4 cycle diesel, but they always ended in the realization that conversion was necessary to reduce compression ratio. This meant a delay due to necessary changes of pistons, addition of electric ignition etc. Even then the engine was a compromise, built to withstand diesel temperatures and pressures and operating on the Otto cycle at lower efficiency. For the past year however, a full diesel, burning gas as fuel has been operating in the municipal plant at Lubbock, Tex. It is an 8 cyl., 1500 hp., 2 cycle, Nordberg, crosshead engine of the air injection type. When operating on gas, the 3 stage injection-air compressor compresses gas instead. At 1100 lb. it is discharged into a common line from which it is admitted to individual cylinders through fuel-injection nozzles equipped with variable lift needle valves. No major change is made in the cylinder for conversion, either fuel using the same pistons, cylinder head, injection nozzles etc. Compression pressure is 475 lb. and gas is injected through the regular fuel-injection valve, to be ignited from the heat of compression in

the normal way. Exhaust is through ports. To obtain smooth operation and uniform combustion, some sort of combustion stabilizer is necessary. Therefore, a small amount of fuel oil is injected with the gas as "pilot oil."

R. H. O.

Buildings Have Pulses.—J. J. CRESKOFF. (*Civil Engineering*, Vol. 7, No. 9.) Buildings are practically always in a state of vibration. This vibration is induced by the action of internal or external forces which may be caused by unbalanced operating machinery, elevators, wind gusts, motor traffic, subway or railroad trains, or earthquakes. No matter how tall and "flexible" or how low and "rigid" the building, it vibrates at pulse rates peculiar to itself. These frequencies of vibration depend on the physical characteristics of the building and its site. They are usually of such low amplitude and frequency that they can be detected only by use of a sensitive vibrograph. But when the period of the actuating force corresponds with the natural or dominant period of vibration of the building, the movements of the latter may become noticeable and even quite alarming to its occupants, although rarely dangerous structurally. Such dominant periods may be discovered by examining vibrograph records of the movements induced in the building by a shaking machine capable of producing impulses of widely varying frequencies.

R. H. O

The Causes of Stain and Decay in Imported Timber.—The Department of Scientific and Industrial Research of Great Britain has published a report by K. ST. G. CARTWRIGHT on this subject describing certain forms of stain commonly encountered, the causes of the various stains, and how it is possible in most cases to decide the time and manner in which they originated. It is stated that discoloration of timber is due to two main causes. They are first, chemical or those that are brought about directly by chemical agencies, and second, biological or stains caused by fungi, or bacteria. The development of stain or decay is dependent upon the presence of moisture in the timber and it is suggested to season the timber to a moisture content below a point at which fungal growth can take place (i.e. below 20–25 per cent. of its oven dry weight) and to protect the timber against re-wetting, in order to prevent deterioration in transit.

R. H. O.

Graphitic Steel.—G. A. STUMPF AND F. R. BONTE give a rather complete story of this material, its fabrication, heat treatment and

application to dies and punches, in *Steel*, Vol. 101, No. 9. This new material, which is a high carbon steel in which a substantial part of the carbon is present in the form of free graphite when the steel is ready for machining, now is being produced commercially by the Timken Roller Bearing Co. for both water and oil hardening applications in the die field. As now produced, the basic analysis of this steel carries approximately 1.50 per cent. total carbon and approximately 1.00 per cent. silicon. It is an electric furnace product, made under rigid control. Ingot size and stripping temperature play an important part in the successful production of this material for once an excessive amount of free graphite has been precipitated, heat treatment will not restore forgeability to the steel. As rolled, but before heat treatment, graphitic steel is a hypereutectoid material composed of pearlite and free cementite with the possible occurrence of finely divided free graphite. Ordinarily only approximately 20 per cent. of the total carbon will appear as free graphite in the steel in this condition, dispersed so finely throughout the steel that no pockets or definitely defined graphitic areas will be noticed. Graphitic steel is now being made in two types, that used for water hardening applications, and that for oil hardening applications, or where distortion must be held to an absolute minimum and where special toughness is required for service.

R. H. O.

Odd Uses of Dyes.—F. HILL in *Chemical Industries*, Vol. 41, No. 2, gives a very interesting description of a great many uses of dyes. Among them are sponges which are now dyed. The natural dark brown coloring matter is first bleached by immersion of the sponges for ½ hr. in 0.25 per cent. potassium permanganate solution. Excess solution is removed by squeezing and the sponges then treated in one per cent. sodium hydrosulfite solution. Finally, they are rinsed in cold water, soaped in a one per cent. soap solution, and dyed with Caledon and Durindone dyes. After dying they are allowed to oxidize for 15 min., and then scoured in warm very dilute acetic acid. Finally they are rinsed well in cold water and soaped for 10 min. in a one per cent. hot soap solution. Another use for dyes is on natural flowers and foliage. Stems of freshly cut blooms are placed in a dye solution, or the blooms are first treated with a solvent which reduces the inter-facial tension between the solution and the petals, and then dipped in the dye solution. The latter method gives greater production; e.g., a few seconds, compared with 4–8 hr. by the capillary method, are needed to yield satisfactory dyeings.

R. H. O.

The Romans Had a Technique For It.—F. E. WERTHEIM in *Heating, Piping and Air Conditioning*, Vol. 9, No. 9, gives some very interesting information on water supply and water piping by the Romans. Rome in the first century not only had a remarkable system of aqueducts, mains and storage reservoirs, but also had a separate group of officials to administer this service. Water from springs and lakes located at distances as great as 60 miles was conveyed by gravity flow to storage tanks built at convenient points within the city; from which, again by gravity flow, it was distributed by lead mains and piping. Roman pipe was made by first casting flat sheets of lead in a mould with a smooth sand floor. These sheets were cut into strips about 10 feet long with a width corresponding to the desired circumference, and were then bent and hammered into pipe form. Opinions differ concerning the shape of the pipe, as to whether it originally was round, triangular, or pear shape. Raised seams were made by filling the tubes with sand and all buried in sand in a manner to form a shallow trough at the seam. It is probable that the edges were preheated by drawing a red hot iron over them, after which molten lead at a temperature at least 50 degrees above the melting point, was poured along the trough, forming a raised longitudinal seam. Crude as this method may now seem, recent hydrostatic tests of some of this old piping have shown that failure did not occur until the pressure of 250 lb. per sq. in. Furthermore, failure did not occur at the seams, which proved to be a source of strength rather than of weakness.

R. H. O.

Sinclair Completes First of Tomato-Type Tanks.—(*Oil and Gas Journal*, Vol. 36, No. 16.) The Sinclair Refining Co. of East Chicago, Ind., has completed the first of several new type gasoline storage tanks. It resembles a huge steel tomato and is completely fabricated by arc welding. The tank is 92 feet in diameter and 47 feet 6 inches high with a capacity of 40,000 bbls. of casinghead gasoline. One of the most important considerations in determining the shape of the new tank, as well as the method of fabrication, was the fact that the structure, when completed, would be subjected to a working pressure of 15 pounds per square inch. Unless high pressure is maintained within the storage tank, the gasoline will boil out. This tank was chosen because it permits the use of tremendous internal pressures. The new tank was tested with a pressure of 17 pounds per square inch.

R. H. O.